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PATE AND TRANSPORT OF LANDFILL CONTAMINANTS,

NAVAL AMPHIBIOUS BASE LITTLE CREEK,

VIRGINIA

by

JAMES M. CONROY

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Departmental Report Civil Engineering

The University of Texas at Austin

in Partial Fulfillment

of the Requirements

for the Degree of

MASTER OF SCIENCE OF ENGINEERING

THE UNIVERSITY OF TEXAS AT AUSTIN

December, 1993

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1.0 INTRODUCTION

Naval Amphibious Base Little Creek is located on the southern shore of the Chesapeake Bay in southeastern Virginia. Originating from this country's preparations for World War II, the base lies at the northwest corner of the city of Virginia Beach, bordering Norfolk. Little Creek was expanded and modernized during the years of the Vietnam War to support littoral and river operations. Because of the changing role of this nation and its Armed Forces in world affairs the importance of amphibious and littoral naval operations is once again increasing in importance.

To continue to provide shore based logistical support to the fleet forces and minimize any potential threats to the environment, U.S. naval installations must identify, investigate and remediate, if necessary, areas which have been contaminated by hazardous substances from past storage, handling or disposal practices. The Naval Amphibious Base Landfill (Site 7) which operated from 1962 until 1979, falls within this category. During these years it was used as the primary disposal site for wastes generated by base operations. The landfill received industrial and municipal type wastes, including many hazardous wastes and the landfill has been identified as a potential source of contamination for nearby groundwater, surface waters and soils. This report considers only the migration of contaminants through groundwater.

The ability to develop a good understanding of the fate and transport of groundwater contaminants from old landfills is usually hindered by a lack of information on the timing, rate, quantities and types of contaminants released into the environment (Taylor, 1986). In some cases this difficulty is overcome by analyzing groundwater contaminant plumes emanating from a landfill. In this case, groundwater flowing beneath the Amphibious Base Landfill is quickly discharged into the adjacent Little Creek Cove, further compounding the problem from both an environmental and investigatory standpoint.

In this report the history and development of the base and landfill are first reviewed to help understand the types and quantities of wastes generated by base operations which were ultimately disposed of in the landfill at Site 7. Information is then presented on the geography, climate,

surface hydrology and hydrogeology of the area and site. This information is relevant to the generation, migration and possible receptors of contaminants from the landfill. A review of details gathered from previous site investigations conducted by the Navy is then discussed.

The next section provides a review of processes which affect the direction, rate and concentration of migrating contaminants and how they pertain to this situation. Following this, the character and generation of contaminants from the landfill is considered. Because of the lack of precise information on the various wastes received at the landfill, the Chemical Oxygen Demand (COD) of the leachate will be estimated and used as an indicator parameter for contaminant modeling. The Hydrologic Evaluation of Landfill Performance (HELP) is used to estimate the quantity of leachate generated and the effects on this from two landfill cover designs. Mercury is used as an example inorganic pollutant to study the processes which can affect the form and mobility of inorganic substances.

Transfer of contaminants to groundwater from non-aqueous phase liquids (NAPLs) will be analyzed. The Hydrocarbon Spill Screening Model (HSSM) is used to evaluate the transfer of benzene and naphthalene from a hypothetical hydrocarbon oil which is lighter than water (LNAPL). A method presented by Pankow and Johnson is applied to denser than water NAPLs (DNAPLs) to examine possible effects from the disposal of this type of waste, using 1,1,1 trichloroethane (TCA) as an example. A groundwater contaminant transport model (UNMOC) is then used to predict the migration of leachate from the landfill, using estimates of leachate COD as an indicator parameter. Finally, recommendations regarding additional characterization of the site hydrogeology are made.

2.0 SITE BACKGROUND

2.1 Base Location and History

Naval Amphibious Base, Little Creek, located in southeastern Virginia's Tidewater region (Figure 1) is a 2,147 acre harbor, industrial, office and housing complex which also includes its

own medical and dental facilities. Little Creek's northern boundary is the Chesapeake Bay, with the cities of Norfolk and Virginia Beach surrounding it on all other sides. Several surface water reservoirs lie to the south and west of the base and are part of the water supply systems for these cities (Figure 2), (Ebasco, 1991).

The Naval Amphibious Base provides logistical support and services to over 25 homeported ships as well as other on base commands and activities. These ships include tank landing ships (LSTs), dock landing ships (LSDs) and salvage ships (ARSS). Little Creek also meets the training and operational needs of several active and reserve amphibious Navy and Marine Corps units. Regional medical and dental centers have been located on base in the past. Permanently assigned base population is near 14,000 with additional personnel arriving during summer months for reserve training. (Ebasco, 1991)

The Amphibious Base was formed in 1945 from the combination of four separate but contiguous Navy facilities. The first of which was formed in 1941 as the United States began to prepare for World War II. From the beginning both heavy and light industrial functions were performed on these sites to support ships operations and training as first light patrol ships and minesweepers were supported and later amphibious ships. Little Creek became a permanent base in 1946 and during the 1950s facilities and utilities systems were upgraded to replace temporary wartime construction. During this time the harbor and coves were dredged to accommodate more and bigger ships. The dredged material was used to fill nearby marshes and lowland areas, including the area to be later used as the Amphibious Base Landfill (Site 7). The 1960s and 70s saw continued expansion and modernization of base facilities to support shallow water and river operations in Southeast Asia. Prior to the early 60s the base operated its own water supply and sewage treatment utilities. Steam for the base heating systems is still generated on base by a coal-fired steam plant. (NEESA, 1984)

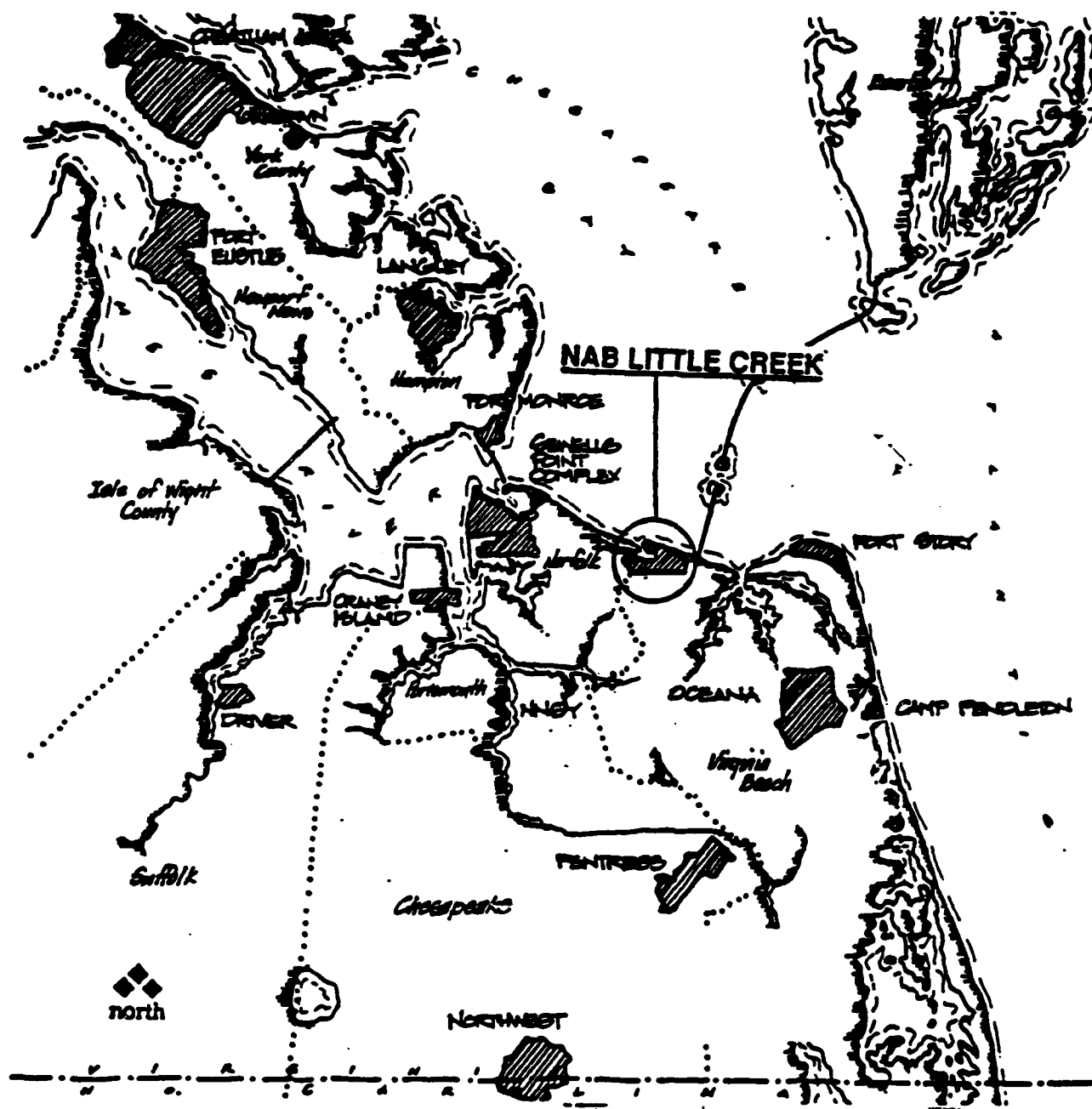


Figure 1. Location of Naval Amphibious Base Little Creek, VA.
Source: Ebasco Environmental, 1991.

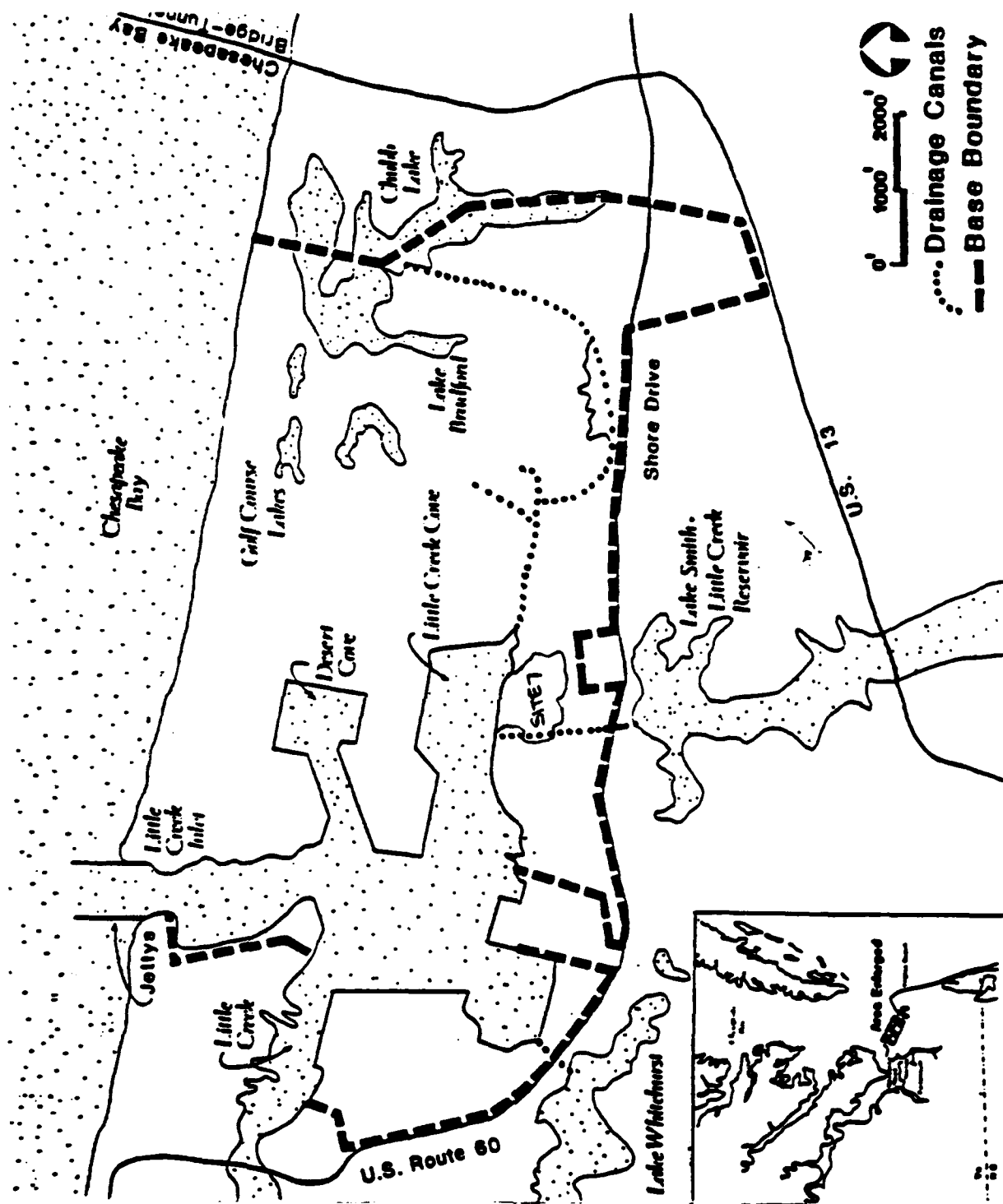


Figure 2. NAB Little Creek and surrounding area.
Source: Ebasco Environmental, 1991.

2.2 Site Location and History

Wastes generated on base during the period from 1962 until 1979 were disposed of in the Amphibious Base Landfill (Site 7). After 1979 wastes were taken off-base for disposal. Because Site 7 served as the only designated waste disposal site from 62-79, it received solid and hazardous wastes generated from on base activities. Site 7 covers approximately 30 acres and received an estimated 500,000 cubic yards of waste, including an estimated 250,000 to 1,000,000 gallons of petroleum lubricants, solvents and degreasers (NEESA 1984). The majority of wastes were similar to a typical mixed industrial and municipal solid waste disposed of during this time, including a significant portion of hazardous materials such as: pesticides, paints, heavy metals, acids, bases, PCBs, solvents, petroleum products and other unknown substances (Ebasco 1991).

The Navy Energy and Environmental Support Activity (NEESA), Port Hueneme, California conducted an initial assessment study in 1984 to identify and assess on-base sites which could pose a threat to human health or the environment from contamination due to past waste disposal practices. This study identified Site 7 as one of six areas needing further investigation. Also at this time, NEESA conducted a base-wide survey of waste generation and disposal practices to be used as a basis for estimating volumes and types of wastes disposed of in the past. Table 1, based on this survey, is a list of various substances disposed of in base landfills. Table 2 provides estimated generation rates for some of these wastes. As can be seen from these lists a large number of industrial and hazardous wastes were disposed of at Site 7. Solid waste volume records were kept from 1975 to 1983 and were also used to estimate volumes of waste generated on base during the life of the landfill.

Site 7 was originally an arm of Little Creek Cove which received dredge spoils before it became a landfill. Figure 2 shows the location of Site 7 in the south-central portion of the base. Figure 3 shows the area in more detail, including the approximate landfill boundary (Ebasco, 1991). The 1984 NEESA study states that the landfill was developed from dry land, underlain by a sandy soil, extending to the west and north into the shallow marine environment of Little Creek Cove, which is underlain by silt and clay soils. Initially, landfilling was a trench and fill operation

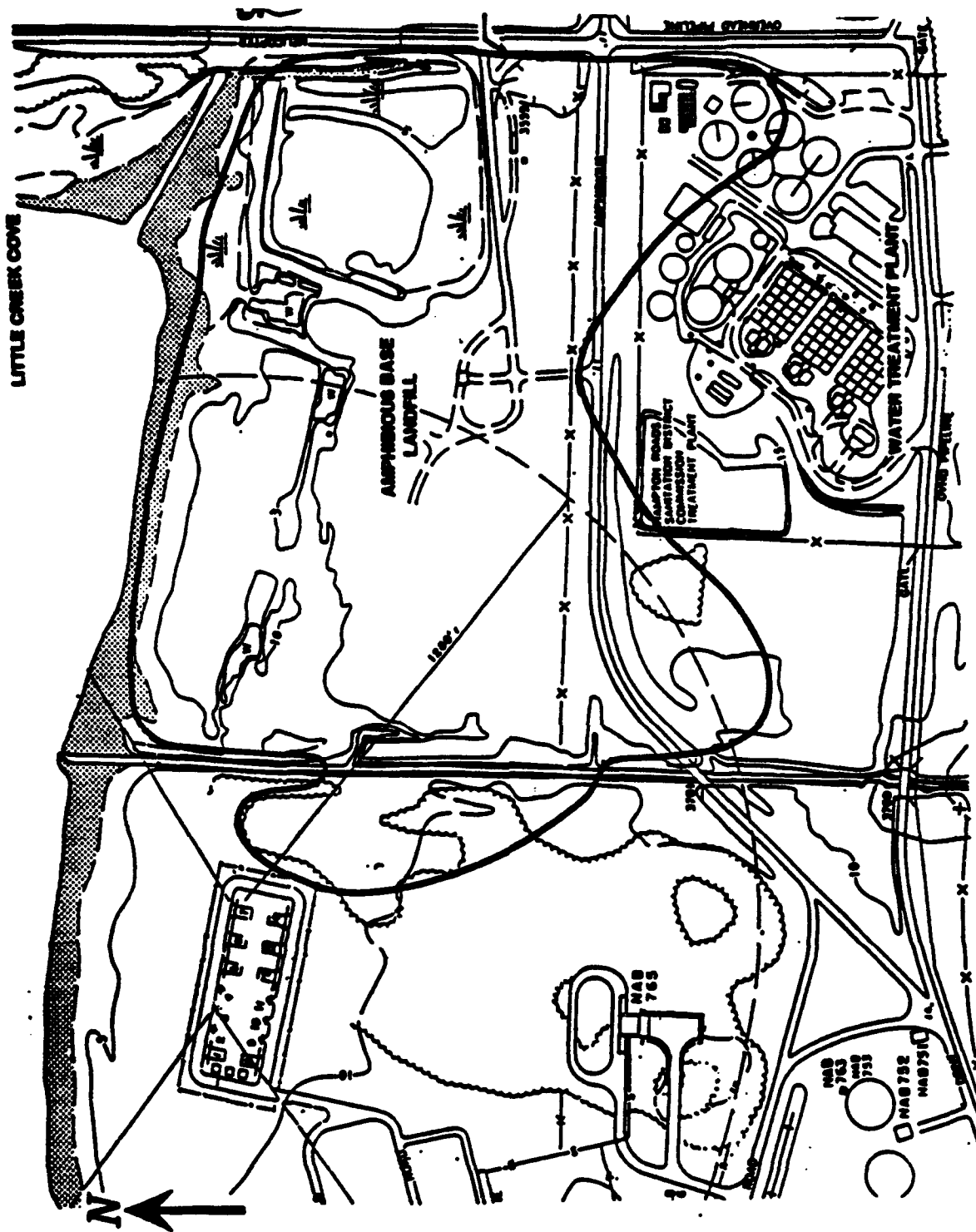


Figure 3. Site 7, Amphibious Base Landfill, approximate landfill boundary.
Source: Ebasco Environmental, 1991

with open burning conducted to reduce the volume of waste. Trenches were excavated to the water table, layers of waste were placed, burned and the remaining portion compacted as best as possible with crawler tractors before cover soil was placed (NEESA, 1984 and Miller, 1993).

Table 1. Substances suspected to have been placed in Site 7 landfill; from NEESA, 1984.

Gasoline (solvent)	Transmission oil
Motor Oil	Degreasers
Batteries	Mercury
Varsol Solvent	Hydrochloric Acid
Sulfuric Acid	Boric Acid
Freon-12	Sulfosilic Acid
Freon-22	Formaldehyde
Oxygen	Acetone
Perchloroethylene (PCE)	Methanol
Paint	Silver Cyanide
Paint Thinner	Copper Cyanide
1,1,1-Trichloroethane	Chromic Acid
Chemical Oxidizers	Nickel Plating Baths
Asbestos	Stripping Acids
Strychnine	Lacquer
Chlordane	Lacquer Thinner
Calcium Cyanide Gas	Enamel
Diazinon	Enamel Thinner
Dalapon	Polyester Resin
2,4-D	Methyl Ethyl Ketone Peroxide
Maleic Hydrazide	Polymer Resins
Cement	Zeptone Alkaline Solution
Diesel Oil	ZEP Degreaser
Coal Ash	ZEP Presto
Liquid Formica	ZEP Dyna Blue
Plastic Resin	ZEP Steam'N'Clean
Pentachlorophenol (PCP)	CALMAL-22
Chromium Paint	CRC-WDC
Muriatic Acid	Hyperchloric Acid
Glue	Sodium Nitrate
Hydraulic Oil	SUBMERGE
JP-5 Fuel	Xylene
Turpentine	Trichloro, Trifluoro Methane
K ₂ CrO ₃	PCB Oils
Solvents	Transformer Cases

Table 2. Estimated annual waste generation rates and total quantities disposed of at Site 7 landfill.

Waste Type	Waste (gal/yr)	Total Qty (gal)
Oils, lubricants, degreasers, solvents	54,000	1,000,000
Gasoline	60	1,080
Paint & Thinner	2,180	39,240
1,1,1-Trichloroethane	620	11,160
Antifreeze	300	5,400
Photographic developing solution	200	3,600
Cyanide solutions, brite dip, nickel plating bath, strippers	60	1,080
ZEP Degreaser	3,220	57,960
ZEP Presto	1,400	25,200
ZEP Dyna Blue	660	11,880
ZEP Steam'n'Clean	275	4,950
CALMAL-22	150	2,700
CRC-WDC	50	900
Hyperchloric Acid	500	9,000
Sodium Nitrate	3,600	64,800
SUBMERGE	600	10,800

Later operations changed to area landfilling with wastes spread, compacted and covered on a regular basis. No reported dates are available as to when this change occurred or when open burning was stopped. Waste oil collection began in 1969 and metal segregation from the waste stream began in 1970. A hazardous waste management plan was implemented in 1979 to keep hazardous wastes separate from the general waste stream. The landfill was closed in 1979, however a portion continues to be used as a staging area for construction debris and metal recycling collection. (NEESA, 1984; Ebasco, 1991)

2.3 Geography and Climate

Little Creek lies within the eastern part of the Atlantic Coastal Plain physiographic region with its characteristic low elevations and low relief. Elevations range from mean sea level along the Chesapeake Bay and Little Creek Cove to a high of 40 feet at some of the larger dunes which make up the natural dune system along the Chesapeake Bay. The average elevation is around 10 feet above mean sea level (Ebasco 1991). The surrounding area consists of industrial,

commercial, transportation and residential development from the cities of Virginia Beach and Norfolk.

The climate of this region is characterized as oceanic with mild winters and moderate summers. The highest monthly average temperature (78.6°F) occurs in July and the lowest (41.4 °F) occurs in January (Soil Survey Report 1988). Average annual rainfall is 45 inches with 8.5 inches of snowfall. Typically there are 244 frost-free days providing an excellent growing season (USGS Soil Survey Report 1988).

2.4 Site Surface Features

Currently the southwestern portion of the landfill is still used as a staging area for construction debris as well as a recyclable metal collection transfer site. This area is maintained free of vegetation while the rest of the landfill is well vegetated with tall grasses and some shrubs and trees. No exposed wastes are evident however settlement of the early trenches does reveal some of their locations. Subsequent area landfilling over earlier trenches could mask the location of more of these earlier operations. The central and southern portion of the landfill is a broad flat area five to eight feet higher than the surrounding areas. Erosion has not been a significant problem since the entire site has fairly flat relief and supports abundant vegetation. A five foot wide discharge canal crosses the western portion of the site, connecting Little Creek Reservoir with Little Creek Cove. This canal is typically dry except for periods of high rainfall when water discharges from the reservoir. (Ebasco, 1991)

2.5 Surface Water Hydrology

The base is bounded on the north by the Chesapeake Bay and is surrounded by several small lakes and reservoirs. The harbor, coves and bay are the dominant hydrologic features. Due to extensive development the base has a broad flat character with an average elevation of 10 feet above Mean Sea Level. The harbor area experiences a semidiurnal tidal fluctuation of 2 1/2 feet (Ebasco, 1991). Overflow discharges from the freshwater lakes reach the cove via unlined canals such as the one which crosses Site 7. Groundwater discharge into the coves and harbors is expected. Most rainfall eventually drains into Little Creek Harbor. Water quality in Little Creek

Harbor is fair. (Applied Environmental 1992)

Little Creek Reservoir lies approximately 1,000 feet south of Site 7. Little Creek Cove borders Site 7 on the north. These features dominate the area surface hydrology. Surface water runoff from Site 7 quickly reaches Little Creek Cove directly or via the discharge canal on the west or a drainage ditch on the east.

2.6 Soils and Geology

Very little undisturbed native soils remain on Little Creek and in the surrounding area. Extensive dredging, filling and development has impacted over 90% of Little Creek; from 1953 to 1956, 12 million cubic yards were dredged from the harbor (NEESA 1984). Development and urbanization of the surrounding area has also left little undisturbed area off-base. Two general soil types occur at Little Creek. Along the coastal areas the soils are formed from aeolian or marine deposits. The remainder of the soils are derived from disturbed material, either from past dredging or other filling operations (USGS Soil Survey Report 1988). The surface soils at Site 7 are of this type, it is loamy and well drained except in the low areas. Underlying most of the area is a sandy soil with some silty sand which transitions to a silty clay near Little Creek Cove (CH2M Hill, 1986).

The geology of the Little Creek area is similar to that of most of the Atlantic coastal plain. Underlying Little Creek is approximately 5,000 feet of unconsolidated marine and fluvial sediments lying on igneous and metamorphic bedrock. The unconsolidated sediments thin in a westward manner. These deposits range in age from lower Cretaceous to recent geologic time. They were formed from nearly continuous depositional sequences as numerous marine transgressions and regressions laid down sediments of varying sizes. This orderly progress was occasionally interrupted by periods of erosion, however the end result is a varied but ordered array of sediments forming layers of aquifers and confining, see Figure 4. The uppermost confined aquifer formation, the Yorktown aquifer, is made up of three of these layers, Figure 5.

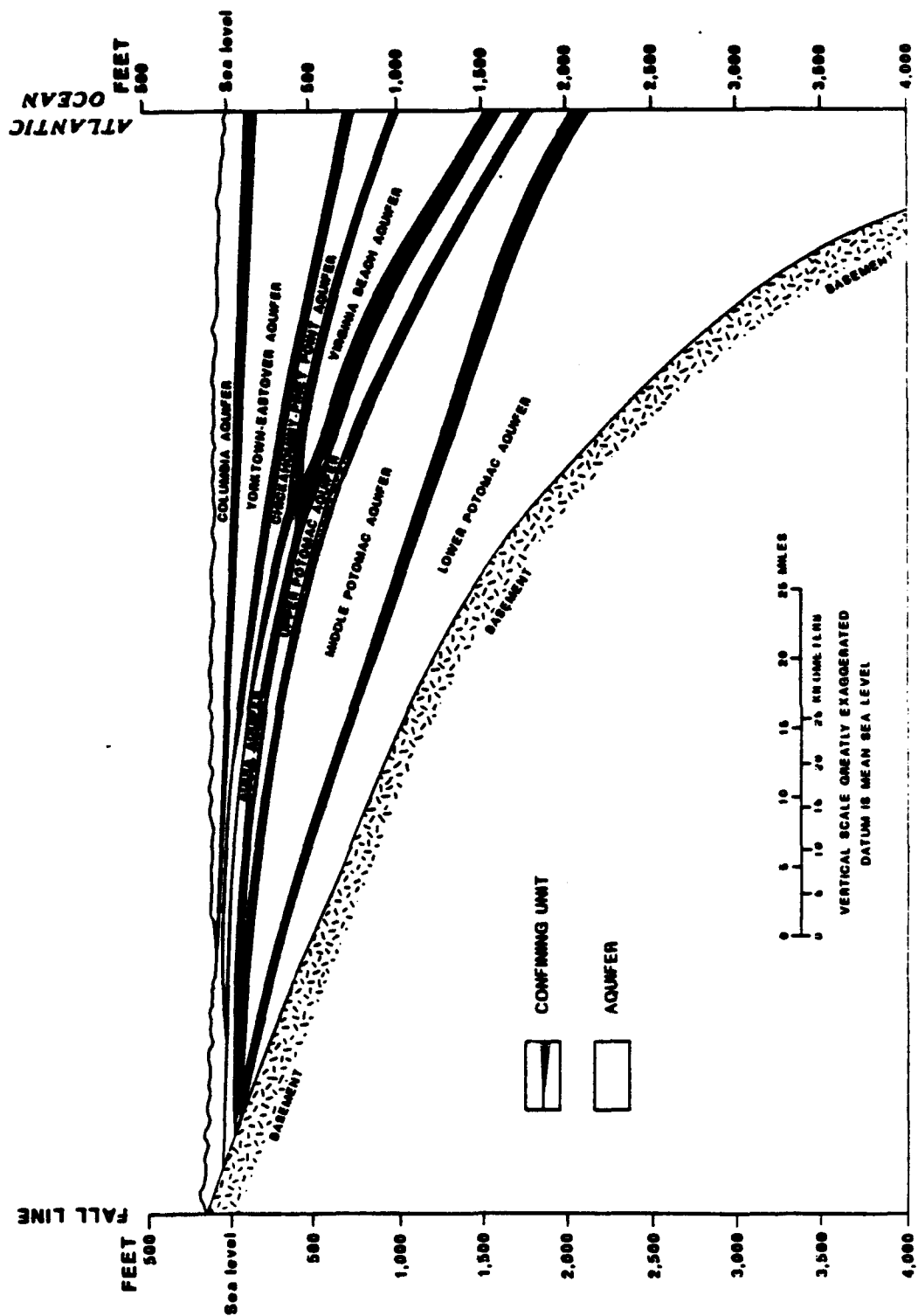
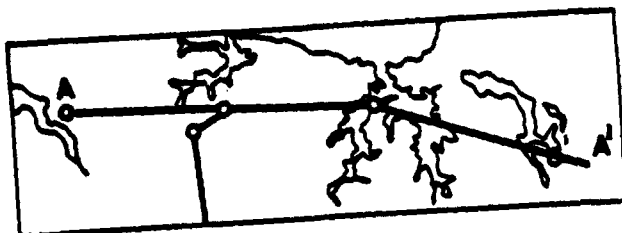
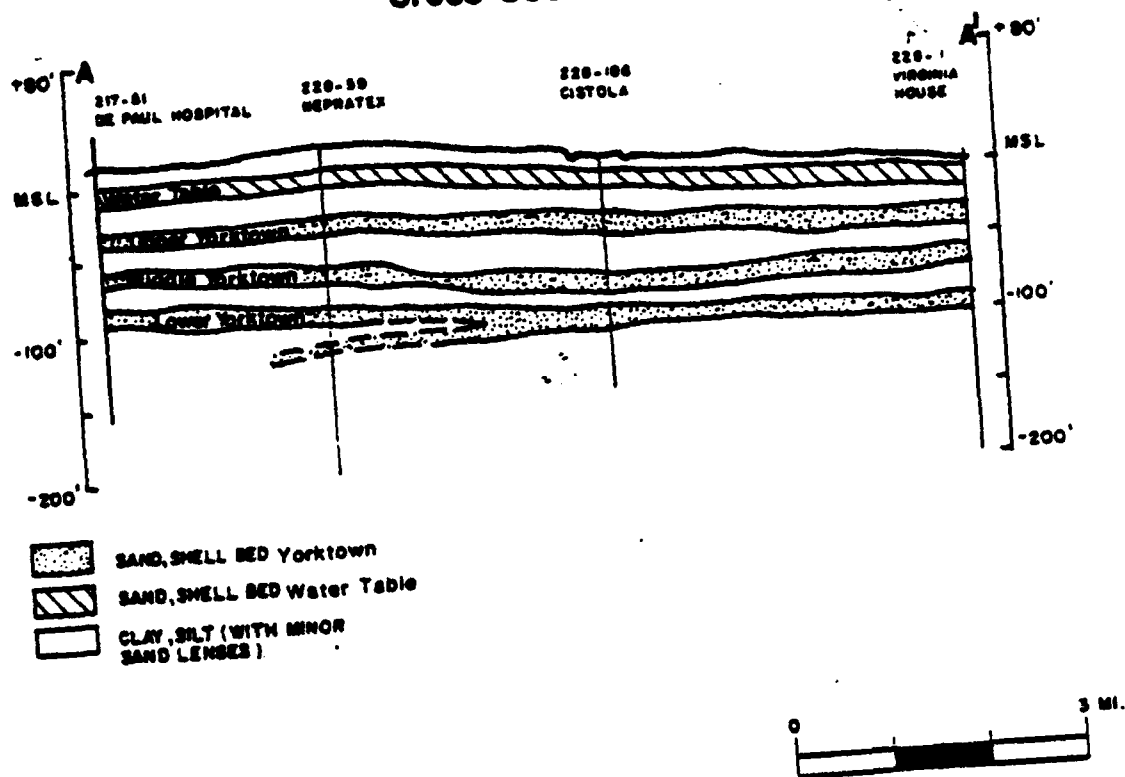


Figure 4. Area hydrogeology. Source: Hamilton and Larson, 1988.



Cross Section A-A'



Source: Sidulya et al., 1981.

Figure 5. Near surface hydrogeologic cross section. Source: Siudyla, et al., 1981.

The unconfined or water table aquifer lies within the Columbia formation which consists of sand and gravel with interbedded silts and clays. The Columbia aquifer is fluvial to marine in origin. (Meng, 1985; NEESA, 1984; USGS Soil Survey, 1988)

2.7 Hydrogeology

At Little Creek the water table aquifer (Columbia aquifer) extends from near the ground surface to a depth of approximately 20 feet below mean sea level. The Columbia is typically unconfined consisting predominantly of sandy deposits which overlie the Yorktown aquifer's confining unit. This confining layer is made up of clayey deposits which are the result of a fining upwards depositional sequence which also formed the coarser deposits of the underlying Yorktown aquifer (Meng and Harsh, 1988). Exploratory borings taken at Site 7 in July of 1993 suggest this confining layer is at least 30 feet thick in that area (Stryker, 1993). Information presented by Meng indicates that this confining layer may be as thick as 45 to 50 feet in the Little Creek area.

Irrigation wells for the base golf course are the only production wells on base utilizing the Columbia aquifer. These wells are not used on a regular basis. Naturally occurring low pH and high chloride and iron levels result in poor water quality in the Columbia Aquifer. No potable water supply wells in the Little Creek area are known to use the Columbia. (Ebasco 1991)

Geologically the Yorktown aquifer is made of three semi-confined aquifer formations, each resulting from marine transgressions which produced shallow bay areas having similar depositional characteristics. Typically the aquifer units fine upwards from a sandy gravel segment to a fine sand and are topped by a fine silty clay confining unit (Meng and Harsh, 1988). The Yorktown aquifer is present at a depth of 50 to 150 feet below mean sea level and is used as a potable water supply. It is believed that the vertical hydraulic gradient between the Yorktown and Columbia aquifers is in the upward direction (Meng and Harsh, 1988).

The Yorktown aquifer (also known as the Yorktown-Eastover aquifer) is not used as a municipal potable water supply source in this area due to considerable local variation in water quality. Little Creek receives potable water from Norfolk's water utility which uses mostly

surface water. The lakes which are directly south of the base are a source of water for the Norfolk system (Siudyla, 1981).

2.8 Previous Investigations

2.8.1 Initial Assessment Study, (NEESA, 1984)

In 1984 the Navy Energy and Environmental Support Activity conducted an Initial Assessment Study (IAS) at Little Creek to identify and assess sites which may pose a threat to human health or the environment as a result of past hazardous waste disposal or hazardous materials operations. The investigation identified 17 potentially contaminated sites. Each was evaluated with regard to contaminant characteristics, migration pathways and potential receptors. Of the 17 sites only six were recommended for further study to confirm the presence or absence of contaminants and to quantify the extent of the problem.

The Amphibious Base Landfill, Site 7 was one of the six sites determined to need further study, the IAS made recommendations as to what steps should be taken. The IAS gathered information regarding the history of Site 7 and developed estimates of the types and quantities of wastes which may have been disposed of at that site. The IAS identified Little Creek Cove and the adjacent drainage canal as potential receptors of contaminants migrating from the landfill, with the Chesapeake Bay as the ultimate receptor. Potential pathways for the contaminants include groundwater and surface water runoff. The recommendations from the IAS were the initial basis for the following work.

2.8.2 Round 1 Verification Step, (CH2M Hill, 1986)

CH2M Hill under contract to the Navy conducted the Round 1 Verification Step at the six Little Creek sites. Monitoring wells were installed at the various sites to allow sampling and analysis of the groundwater. The monitoring wells were also to provide hydraulic head information to determine groundwater flow directions. Surface water and sediment samples were taken to determine the impact on nearby surface water bodies from the sites and to determine if

surface water runoff was contaminated due to contact with the sites.

Nine monitoring wells were installed around Site 7 as shown in Figure 6 (taken from Ebasco, 1991). This figure also shows the expected groundwater flow at this site based on water levels in the monitoring wells. Soil boring logs and well construction data for the monitoring wells are shown in Appendix A. One groundwater sample was taken from each well and five surface water and five sediment samples were also collected. The surface water and sediment samples were collected from the drainage canal and along the cove shoreline. Most organics compounds tested for were below method detection limits however low concentrations of some compounds were found. Inorganics found at high levels were selenium, silver, thallium, lead and nickel. The elevated levels of Se, Ag, Th, Pb and Ni along with elevated levels of total petroleum hydrocarbons were found in the monitoring wells along Little Creek Cove; GW7, GW8 and GW9.

pH, Eh (mV), conductivity and temperature measurements were taken prior to collection of groundwater samples. The Eh measurements range from -64 to -214 mV, indicating a slightly reduced environment. pH ranged from 6.2 to 7.4. Electrical conductivity was much higher at monitoring wells GW7, GW8 and GW9, suggesting saltwater influence from the cove resulting in higher ion concentration.

Because few contaminants found were at seriously elevated levels, CH2M Hill concluded that little or no contamination was leaving the landfill at that time. The report also concludes that groundwater was the primary migration pathway of concern. However they cautioned that because of the uncertainty in the nature, quantity and extent of contaminants disposed of in the landfill, unrecognized migration pathways could exist.

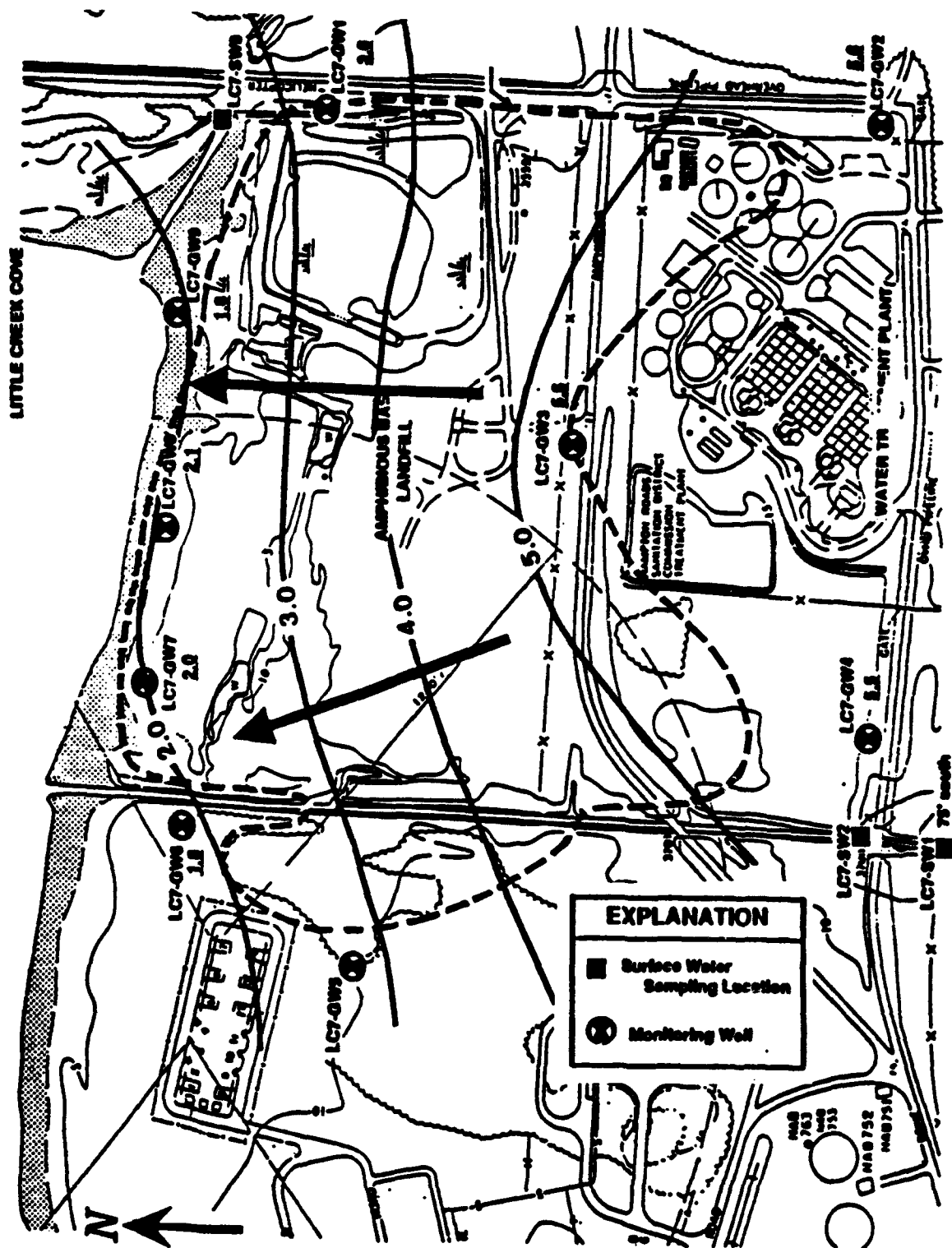


Figure 6. Site 7 monitoring well locations and water table elevation.
Source: Ebasco Environmental, 1991.

2.8.3 Interim Remedial Investigation, (Ebasco, 1991)

Earlier work had been conducted under the Navy Assessment and Control of Installation Pollutants (NACIP) program. This program was replaced by the Installation Restoration Program which is the reason for the change in titles for this stage of work. During this investigation conducted by Ebasco Environmental of Arlington, Virginia, twelve groundwater and eleven surface water samples were collected, groundwater levels were also determined. Sample locations are shown on Figure 7. Results of the water table level determination is shown in Figure 6. During this investigation monitoring well GW5 could not be found. It is suspected to have been covered or removed during construction on a nearby area. Nine unfiltered groundwater samples were taken in December 1990 and three filtered were collected in March 1991.

Figure 6 shows that the groundwater in the water table aquifer is flowing beneath the landfill and discharging into Little Creek Cove. Little Creek Reservoir provides a nearly constant head source to drive the water flow toward Little Creek Cove which is at a lower elevation. The hydraulic gradient in this area is approximated as 0.0018. Ebasco draws the conclusion that discharge into the cove occurs along a zone parallel to the shoreline because of the high chloride content in the monitoring wells in this area, indicating influence of the salt water cove on the groundwater.

Analyses of the samples included testing for Target Compound List (TCL) volatile organic compounds (VOC), TCL semivolatile organic compounds (SVOC), TCL pesticides, and polychlorinated biphenyls (PCB). Also, total and dissolved Target Analysis List (TAL) metals, ethylene dibromide (EDB), total petroleum hydrocarbons (TPH), total organic carbon (TOC), hexavalent chromium, sulfate ions, chloride ions and alkalinity. No organics were detected in the monitoring wells except for naphthalene which was found in an upgradient well (GW4). This compound was not attributed to the landfill. TOC levels were higher in the wells near the cove but did not exceed 21 ug/L.

Analysis for inorganic contaminants found elevated concentrations of several inorganics in the unfiltered samples: (arsenic, 55 ug/L; cadmium, 33.5 ug/L; chromium, 178 ug/L; and lead,

84 ug/L. The corresponding Maximum Concentration Levels (MCL) are As - 50 ug/L, Cd - 5 ug/L, Cr - 100 ug/L and 5 ug/L for Pb. The filtered samples however detected none or low concentrations of these metals. Filtering removed particles greater than 40 microns in diameter. This indicates that the metals are associated with the suspended sediments of larger size and are relatively immobile. Chloride and sulfate concentrations were high for the wells near the cove and decreased with distance away from the cove. Alkalinity was also higher in these wells.

Ebasco concluded that the contaminant pathways of concern were through contact with soil particles at the unvegetated portion of the landfill and through contact with surface water and sediment exposed to the site. Because there is no existing use for groundwater at this site they concluded that this was not a pathway of concern.

Based on the their own and previous groundwater testing Ebasco concludes that Site 7 is not an active source of groundwater contamination. Recognizing that the cover material is permeable and that the landfill is most likely still generating leachate they further conclude that the leachate is either free of contaminants of concern or is being diluted to concentrations below detection limits. Their final recommendations are to close the landfill in accordance with Virginia requirements and provide annual groundwater monitoring until 2009 (30 years after landfill operations ceased).

2.8.4 Background Water Quality Study (Applied Environmental, 1992)

This study was conducted in 1992 to establish background water quality and groundwater conditions at Little Creek. The data from this study is needed for the preparation of environmental risk assessments and groundwater cleanup standards at contaminated sites. Sample locations were chosen base-wide and avoided suspected or known contaminated sites. Pump tests were conducted at two of the sites to determine hydraulic characteristics of the water table aquifer. Ten groundwater monitoring wells were installed for this study.

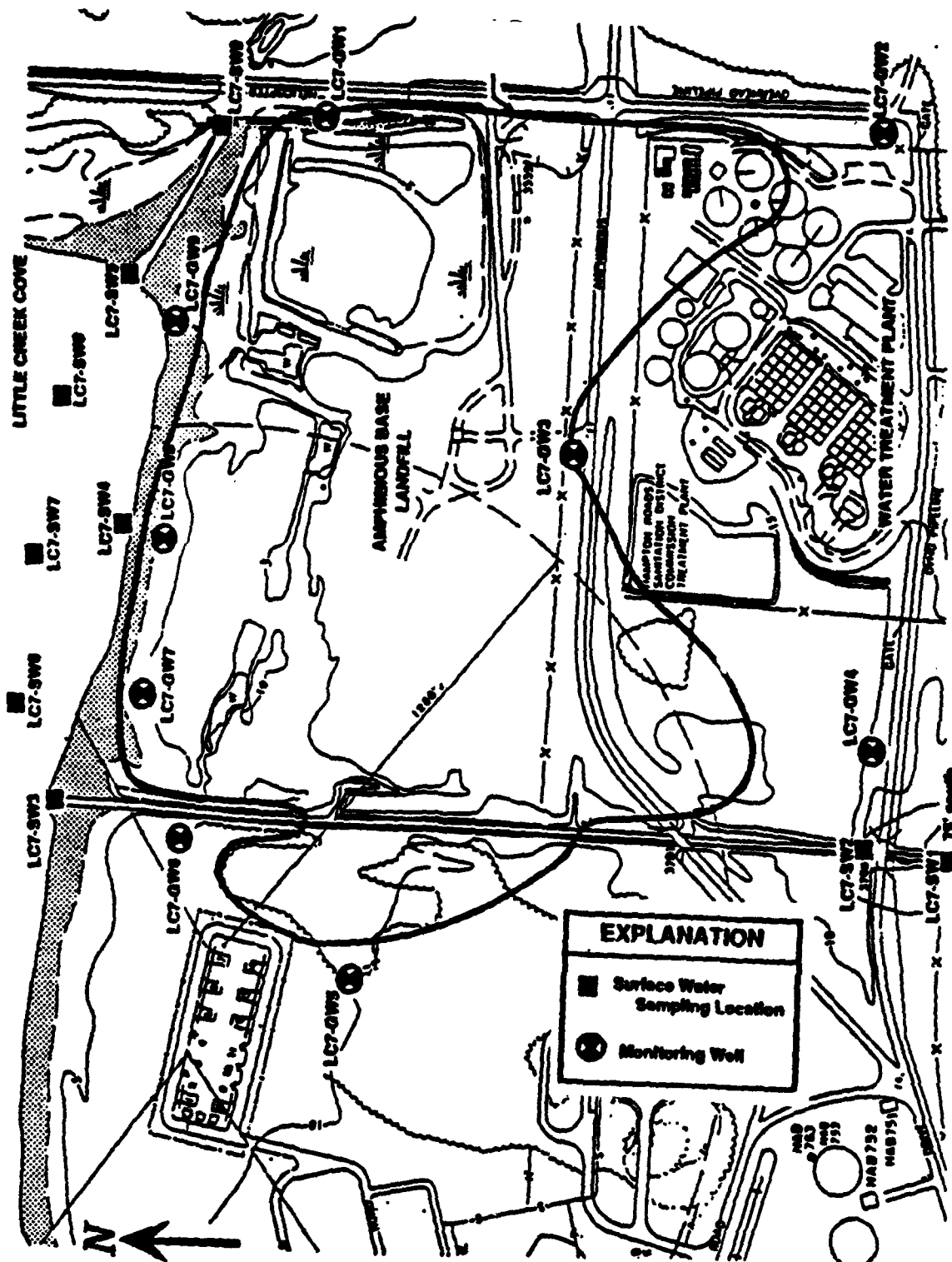


Figure 7. Site 7 sampling locations. Source: Ebasco Environmental, 1991.

Very few organic contaminants were detected and those that were found (except two) were at concentrations of 2 ug/L or below. Sample pHs were in the 5 to 7 range. Groundwater quality did not appear to be impacted by operations at the base. However, high concentrations of aluminum (2.4 mg/L average), iron (6.9 mg/L average) and manganese (0.3 mg/L average) make the water unsuitable for drinking. The installed monitoring wells and pump tests at two locations provided the following information:

Hydraulic gradient 0.0007 to 0.010 ft/ft,

Coefficient of transmissivity 10,400 to 116,500 gpd/ft,

Hydraulic conductivity 110 to 1,300 ft³/day-ft²,

Groundwater velocity 0.4 to 4.6 ft/day.

Using these values a calculated value for the effective porosity is approximately 0.3.

2.8.5 Recent Work

In October of 1992 additional surface water and sediment samples were taken from the drainage canal along the western side of Site 7. These efforts were in support of development of an inter-tidal wetland treatment system to possibly be constructed at the point the drainage canal outfalls into Little Creek Cove. High levels of heavy metals were found in the sediment samples, including concentrations of mercury as high as 210 parts per billion (ppb). This has raised concern over the migration of these contaminants from the landfill.

In June and July of 1993, three borings were completed to determine the thickness of the Yorktown confining unit underlying the Columbia (water table) aquifer at Site 7. The first boring stopped ten feet into the confining layer, the second at twenty feet and the third stopped at thirty feet. This would indicate that the confining layer is at least thirty feet thick under the landfill. Because of the depositional nature of this layer the confining unit is probably uniform in thickness under the landfill. Additionally, during this period the effects of tidal fluctuations in Little Creek Cove on groundwater at Site 7 was studied. Reports from these last two efforts were not available as of this writing.

3.0 CONTAMINANT MIGRATION

The impact of improper disposal of hazardous materials centers around the questions of where the contaminants will migrate to, how long will it take to reach the receptor, what concentration will be seen at the receptor and will transformations have occurred to the substance along the way. Transport of the contaminants through groundwater (ignoring vadose zone transport) is responsible for the first three questions. Contaminants in the aqueous phase move with the flow of groundwater and are subject to many processes which alter their movement with respect to that of the water itself. Some of these processes are: dispersion, diffusion and sorption. Transformations can occur as organic substances undergo biological conversions or as inorganics participate in acid-base, oxidation-reduction, dissolution, precipitation or complexation reactions. These transformations can drastically change the chemical as well as its mobility characteristics.

3.1 Advection, Dispersion and Diffusion

Advective or bulk transport describes the movement of substances with the flow of the groundwater unaffected by other processes. This would be described by an "ideal" plug flow model neglecting longitudinal and lateral mixing. Given a continuous source of contaminant, it would move as a sharp concentration front, going from background concentration levels to that of the source in an immediate jump. Longitudinal dispersion and diffusion act to displace some of the dissolved substance to move ahead of the advective front. This causes the front to act as a breakthrough curve instead of a sharp front, with some of the substance reaching a point faster than groundwater flow. Some distance behind the breakthrough curve the concentration reaches the source strength the same as for advective flow alone. Lateral and vertical dispersion cause spreading of the substance in these directions. This results in a lowering of the concentration from that at the source.

Molecular diffusion causes a substance in solution (solute) to move from high to low concentrations. Diffusion will occur as long as concentration gradients exist and does not require fluid flow to occur. However, except in very slow flowing groundwater, diffusion effects are

several orders of magnitude less than those due to dispersion. Dispersion of a solute in advective flow results from the different flow paths water must take as it moves through porous media. Some particles of the solute will take shorter or longer paths, water and solutes will travel faster through the center of pore spaces than along the edges and water will travel faster through larger pores than smaller pores (Fetter, 1993). All this results in a mixing and dilution of the concentration front, termed mechanical dispersion. This dispersion occurs in the direction of flow (longitudinal dispersion) and in directions normal to flow (transverse dispersion).

The effects of these two processes, diffusion and mechanical dispersion, are difficult to differentiate and are usually combined into a single parameter, the hydrodynamic dispersion coefficient (D_i), where the subscript i indicates the direction: longitudinal, transverse or vertical. Dispersion is a function of the groundwater velocity multiplied by a dispersivity term. Dispersivity is determined by the properties of the porous media and fluid but is also proportional to flow scale, i.e. the longer the flow distance the greater the dispersivity. Dispersion is generally orders of magnitude greater in the direction of flow than in transverse directions and can be determined using field tracer tests.

3.2 Sorption

Sorption processes are those that somehow bind a contaminant to solid particles of the porous media, including: adsorption, chemisorption, absorption and ion exchange (Fetter, 1993). Sorption serves to slow the migration of a substance relative to the velocity of the groundwater. The ratio of the groundwater velocity (v_w) to that of the contaminant (v_c) is known as the retardation factor (R_f).

Ion exchange may occur as cations are attracted to the negatively charged flat surfaces of clay minerals or anions are attracted to the positively charged sites on iron or aluminum oxides or the edges of clay particles which are also positively charged (Fetter, 1993). Adsorption can occur when hydrophobic organics are adsorbed onto the organic fraction of the porous matrix. Inorganics may also be adsorbed to the porous media, e.g., trace metals adsorbed to silica sand (Leckie, 1974). Chemisorption takes place when the substance is bound to the solid surface due

to a chemical reaction. If the solid particles are porous, the dissolved substance may diffuse into the solid and be absorbed inside.

The ability of a solid to sorb a substance in solution is in part a function of the concentration of the substance in solution. This phenomenon is modeled in several ways, based on various assumptions. Sorption may be modeled as being in equilibrium using an equilibrium isotherm model or if equilibrium is not readily achieved a kinetic sorption model may be needed. Linear and non-linear isotherm models have been developed for both equilibrium and kinetic cases. Several of these models are discussed by Fetter (1993). In this modeling effort the simple linear equilibrium isotherm model will be used since little information regarding the sorption characteristics of the aquifer and contaminants is known to justify a more detailed approach.

The linear sorption isotherm relates the concentration sorbed on the soil to that in solution with the following equation:

$$C_s = K_d * C_{aq}$$

where: C_s = concentration in the solid phase (mg contaminant per kg soil),

K_d = slope of sorption isotherm,

C_{aq} = aqueous phase concentration.

For hydrophobic organic compounds which sorb onto the organic fraction of the aquifer solids:

$$K_d = K_{oc} * f_{oc}$$

where: K_{oc} = organic carbon partition coefficient,

f_{oc} = fraction of organic carbon in aquifer solids.

K_{oc} has been related to the hydrophobicity of organic compounds by several investigators (Fetter, 1993). An appropriate K_{oc} for the particular contaminant may be determined from a review of available information in the literature.

Once K_d is known the retardation factor can then be computed as:

$$R_f = 1 + (p_b/n)K_d$$

where: p_b = bulk density of aquifer solids,

n = porosity.

Because hydrophobic organics sorb to the organic fraction of the aquifer solids, there is concern that the high concentration of dissolved organic carbon (DOC) found in landfill leachate may also sorb these pollutants, making them more mobile. Larson, et al. (1992) studied the effects of DOC in landfill leachate on the sorption of these pollutants onto aquifer solids. They found that the hydrophobic organics did sorb onto the leachate DOC, potentially increasing the mobility of these contaminants. However, the exposure of the aquifer solid matrix to landfill leachate also increased the ability of the aquifer solids to sorb the hydrophobic organics. These off-setting effects were found in some cases to increase mobility and in others mobility decreased. No clear conclusions were drawn by their studies except that the presence of landfill leachate did alter the sorption interactions between hydrophobic organics and the organic fraction of the aquifer solids. This effect was more pronounced for the more hydrophobic compounds.

Metals may become bound to solids through cation exchange, precipitation, sorption, or complexation reactions. Retardation of metals will be significantly affected by pH and Eh as these parameters control the form in which the metals will exist. If conditions favor a metal form which will precipitate then mobility will be greatly reduced.

Overestimating the retardation factor will result in a slower moving contaminant plume and dilution within the plume will be slowed. In situations where the history of the plume source is known and detailed information on concentration gradients of various contaminants is known, apparent retardation factors can be estimated from the rate of movement of a particular contaminant with respect to that of a conservative substance like chloride. Chloride does not tend to be affected by sorption or degradation processes and can be used to estimate groundwater velocity.

3.3 Transformations

Biodegradation of organic substances in groundwater may occur through aerobic, anoxic or anaerobic pathways depending on the presence of molecular oxygen and the redox potential. In the absence of oxygen microorganisms must use other substances as electron acceptors, such as; nitrate, iron and manganese oxides, sulfates, carbon dioxide or organic molecules. Adequate nutrients and microbial populations must exist for the degradation to be significant. Substances

which are toxic to particular microorganisms may interfere with the process. Degradation can often be approximated as a first order kinetic reaction and an effective loss rate constant or half-life determined.

Jackson et al. (1992) propose three potential anoxic pathways for the biodegradation of 1,1,1 trichloroethane (TCA), shown in Figure 8. This illustrates the importance of understanding the degradation processes and possible intermediate compounds. In this case, vinyl chloride a highly carcinogenic substance is formed as an intermediate to one of the possible pathways. It is also necessary to understand what redox condition, pH, nutrients and other requirements are necessary for a particular contaminant to biodegrade under different pathways.

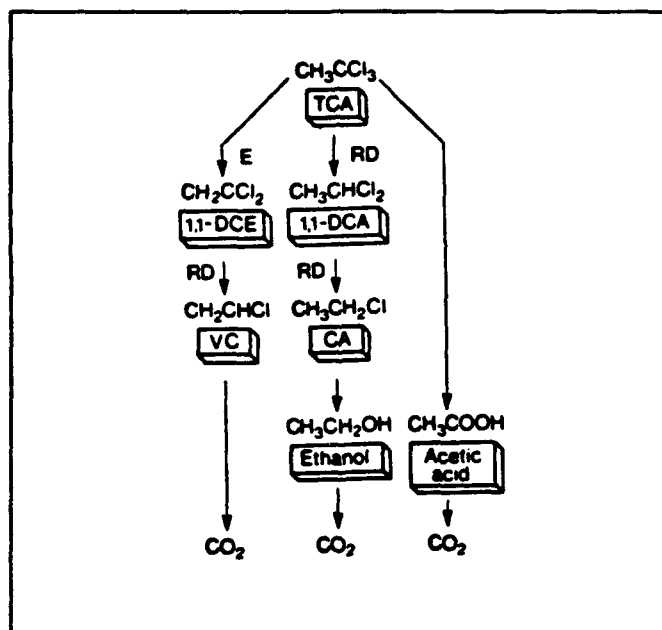


Figure 8. Potential biodegradation pathways for TCA.

Source: Jackson, et al., 1992.

DeLaune and Pardue (1991) present optimal redox conditions favoring degradation of toxic chlorinated organics, petroleum hydrocarbons and pesticides. Most favor an oxidized (high Eh) environment, however, some require a reduced (negative Eh) condition. Kinzelbach (1985) reports a TCA half-life of 3500 days in a plume from a chemical plant in Germany. The plume is within the water table aquifer and consists mainly of TCA. Evaluation and numerical modeling of

the plume where used to determine the apparent half-life and a retardation factor (~ 1) in this sand and gravel aquifer. The pH, redox potential or degradation byproducts were not reported.

Mackay and Vogel (1985) report both anaerobic biodegradation and chemical transformation of TCA. Estimated half-lives for chemical transformation of TCA resulting in 1,1-dichloroethene (DCE) ranged from 0.5 to 0.8 years. Half-lives for chemical transformation resulting in acetic acid ranged from 0.7 to 1.7 years. Anaerobic biodegradation of TCA to 1,2-dichloroethane (DCA) had a half-life reported at 0.7 years. Mackay and Vogel also reported aerobic and anaerobic biodegradation of benzene resulting in production of carbon dioxide with a half-life of 0.2 years.

Spillman (1989) describes a research project in Germany which studied the biodegradation of landfill leachate and various organic compounds added to the leachate; chlorphenol, Lindane (a pesticide) and two chemically similar herbicides (Atrazine and Simazine). The research study used four trenches (100m x 1.2m x 1.2m) which were excavated, lined and filled with clean sand similar to many water table aquifers in Germany, Figure 9 (e). Flow was maintained in these artificial aquifers and landfill leachate was added. Chemical Oxygen Demand (COD) and concentrations of the organic compounds was monitored along the trench to determine the rate of degradation, Figure 9 (a). Biological activity was monitored by bacterial counts from within the trenches, Figure 9 (b), mainly facultative bacteria were found to be present. Measurement of acid phosphatase was used as a measure of the biochemical activity, Figure 9 (c). The amount of total humic material present is shown in Figure 9 (d).

Fresh leachate with a high COD was quickly biodegraded with a reduction of approximately 70% of the COD within the first 30m. After that the rate of reduction was much slower, with another 5 to 10% reduction in the remaining 70m. An old leachate which had a low COD was reduced at a steady but slow rate over the entire 100m. Bio-activity was similar for both cases as measured by bacteria count and acid phosphatase concentrations. When the organic chemicals were added to the leachate flow chlorphenol and Lindane were quickly eliminated while Atrazine and Simazine showed no degradation.

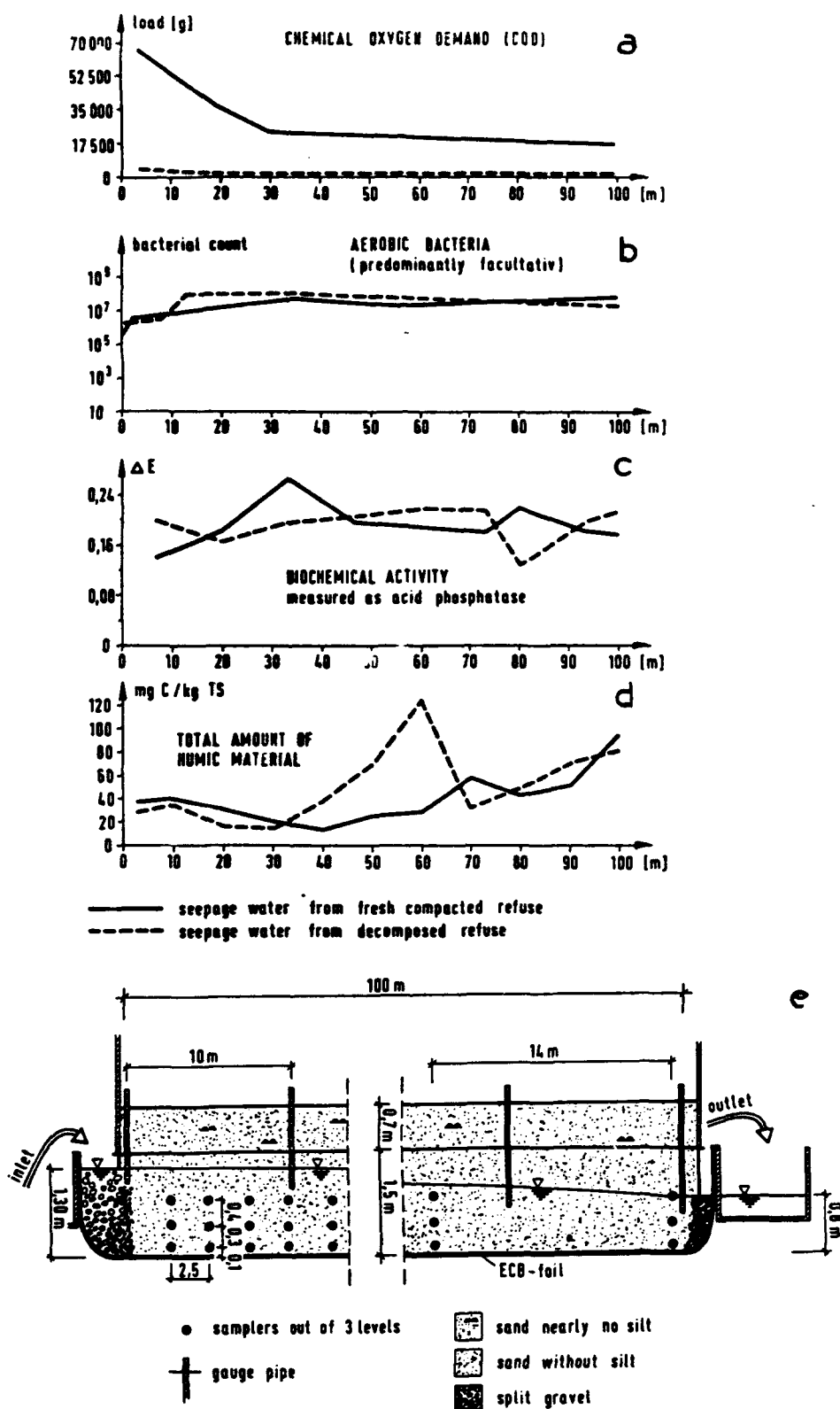


Figure 9. Artificial aquifer and characteristic indicator parameter curves of biochemical decomposition. Source: Spillman, 1989.

Landfill leachate is derived from an environment where active biodegradation of organic substances within the landfill is occurring. As shown by Spillman (1989), this results in the leachate having a high level of microbial activity as it reaches and travels through the groundwater. Nutrients from the hydrolyzed organics from within the landfill continue to provide nutrients within the leachate. In the absence of toxic substances which would suppress microbiological activity it would be surprising if biodegradation of organic contaminants in the leachate from Site 7 was not occurring. However without being able to quantify these transformation it is difficult to include them in a site assessment. The effect of biodegradation will be considered during computer simulation of groundwater contamination at Site 7 by using a range of "reasonable" half-lives.

3.4 Parameter Estimation

Aquifer hydrogeological parameters are needed to determine the groundwater flow field. Knowledge of hydraulic gradients, aquifer thickness, hydraulic conductivities, porosity, storativity or specific yield, and the presence of preferential pathways are all necessary to adequately determine contaminant migration. These parameters are usually assumed to be constant over a large area but in reality may vary greatly in short distances. Extensive field investigations may be required to be able to describe these parameters with some confidence. Contaminant transport parameters including; dispersivities, retardation factors, degradation half-lives and chemical properties of the contaminants themselves must also be determined for transport modeling. The quantity of contaminant and the manner or rate it was released also may greatly affect migration.

Commonly the contaminant plume can be used to estimate values of transport parameters. Transport models can be used to with available information and the parameters are calibrated to match the migration history of the plume. This can provide information on lateral and longitudinal dispersion. The differential migration of contaminants within the plume can furnish estimates of retardation factors. By comparing the speed of migration of contaminants to that of a conservative substance, like chloride, which moves at or near the groundwater tracer velocity actual field values of R_f can be determined if accurate information is available.

Modeling contaminant transport at old landfill sites is complicated by a lack of knowledge regarding the types and loading rates of contaminants. Using the hydrogeologic and transport parameter information available, ranges of values can be estimated for the unknown parameters based on previous modeling and research studies available in the literature.

The flow of groundwater and contaminants are interrelated, changing hydraulic parameters changes not only groundwater flow but also the rate of plume migration. Changes to longitudinal and transverse dispersion affects the rate at which the contaminant spreads. Slower migration of a plume keeps it in a tighter configuration with higher concentrations. Frind and Molson (1989) contend that migration of contaminants is to a large degree controlled by the three-dimensional groundwater flow system and that understanding this should be the first priority in data gathering. As more information becomes available on a particular site then modeling efforts can be refined. At Site 7 this could be accomplished with geophysical methods to evaluate the extent and impact of the aquifer variability on the plume migration. Existence of preferential pathways would invalidate any results from modeling assuming a homogeneous aquifer.

Parameters for the following modeling efforts on Site 7 will be based on previous site studies and regional hydrogeological reports as well as estimates based on values reported in the literature. One disadvantage to this site is the nearby groundwater discharge area, preventing development of a plume which could be evaluated to help determine estimates of hydrogeological information such as groundwater velocity, dispersivities and retardation factors.

4.0 LANDFILL CONTAMINANTS

Disposal of waste materials in landfills presents the potential for some of these materials to migrate to adjacent areas. Possible receptor media include air, soil, surface waters and groundwater. Leachate, generated by the movement of water from or through the wastes, can carry into groundwater a wide variety of organic and inorganic constituents. In unlined landfills such as Site 7, there may be little resistance against the movement of aqueous phase contaminants

or separate non-aqueous phase liquids (NAPLs) into the surrounding space. The following discussion will cover the generation and composition of leachate including inorganic constituents. The development of Chemical Oxygen Demand (COD) as an indicator parameter to model leachate is discussed and mercury is examined as an example of an inorganic contaminant.

4.1 Leachate

Leachate is produced as water comes into contact with the landfilled wastes moving contaminants into the aqueous phase. Once the field capacity of the waste is exceeded, leachate flows downward until it is incorporated into the groundwater. At Site 7 where waste was placed at, or perhaps slightly below the water table, leachate is quickly mixed with groundwater. In an effort to understand the quality and quantity of leachate generated at Site 7, factors affecting the generation, composition and migration of leachate are discussed below.

4.1.1 Leachate Generation

Sources of water which may enter a landfill and contribute toward leachate production include: water within wastes, infiltration from precipitation, surface water run-on, intrusion of groundwater, biological conversion of organic wastes and consolidation of waste and soil layers. Except for wastes which are placed in a landfill with very high water contents, such as sludges, the quantity of leachate produced is controlled by the amount of water entering the landfill from external sources (Schroeder, 1984).

As water moves through the waste it picks up contaminants by several mechanisms. Contaminants can be mobilized into the water by dissolution or suspension. As the organic portions of the waste decomposes due to biological action, metabolic intermediates and end products can be taken into solution or suspension (Farquhar, 1989). These products can increase the ability to leach metals due to lowered pH and their ability to complex with metals (Lu, 1985).

The quantity of leachate produced from a landfill varies considerably with climatological factors and design and operating practices. Precipitation reaching the landfill cover will run off or infiltrate through the cover soil. The water which infiltrates may fill a water deficit, if the soil moisture content is below its field capacity, be returned to the atmosphere via evapotranspiration

or percolate down through the waste layers. If the moisture content of the waste layers is above field capacity, leachate will be produced. The leachate will continue down through the unsaturated zone, if it exists, until it reaches the water table. This assumes there are no "perched" aquicludes and that the soil mass does not have the capacity to store all leachate produced. Leachate from Site 7 may directly enter the groundwater because of the high water table.

Leachate production varies greatly at different sites and even over time at the same site. Climatological factors such as precipitation, temperature, windspeed and humidity establish the availability of water for leachate generation by determining the amount water supplied to the site and affecting the loss rate due to evapotranspiration (Lu, 1985). The type of cover soil and vegetative cover affects surface runoff and evapotranspiration losses.

Cover soil characteristics such as hydraulic conductivity (as a function of water content) and moisture retention capability determine the infiltration rate for a given availability of water at the surface. The elevation of the water table with respect to the landfill and the groundwater flow patterns determine the amount of groundwater intrusion.

Several mathematical and computer models, using either mass balance or numerical methods, have been developed to estimate the amount of leachate generated within a landfill. The U.S. Army Corps of Engineers Hydrogeologic Evaluation of Landfill Performance (HELP) model was developed as a design tool which would evaluate the effects on leachate production of various design alternatives and assist in regulatory review of landfill designs (Schroeder, 1984). This model is used to develop an estimate of the volume of leachate produced at Site 7 and the effects on leachate production of a landfill cap, see section 4.1.5.

4.1.2 Leachate Composition and Characteristics

Landfill leachate is derived from water infiltrating through layers of waste. The composition of leachate is dependent upon the content of the original waste, biological and chemical decomposition reactions, landfill age and the amount of water passing through the waste. Other factors which also affect leachate composition are: in-place density, degree of waste processing (shredding or baling), burning of wastes, thickness of waste and waste

temperature in the landfill.

Leachate forms as infiltrating water extracts soluble organic and inorganic substances and takes particles into suspension, resulting in a solution similar to a high strength wastewater. Conversion of biodegradable organic matter to gases (CO_2 and CH_4), water and soluble organics also adds to the composition of the leachate. Chemical Oxygen Demand (COD) concentrations have been reported as high as 100,000 mg/L (Lu, 1985), Total Suspended Solids (TSS) as high as 1,000 mg/L (Harris, 1989) and Total Dissolved Solids (TDS) as high as 45,000 mg/L (Lu, 1985).

Many investigators have studied leachate from municipal solid waste landfills (MSW), mixed industrial and municipal landfills, hazardous waste landfills, field lysimeter tests and laboratory column tests. As one would expect given the variables involved, leachate composition values vary to a large degree. One study of 24 landfills owned by the same corporation found highly variable water chemistry parameters in the leachate produced (Harris, 1989).

Microbial biodegradation of landfill organic materials begins as an aerobic process but the limited available oxygen is quickly consumed. Biodegradation continues under anoxic conditions as the microbes utilize nitrates, sulfates and other electron receptors (Farquhar, 1989). This phase continues rapidly if moisture is available. Organic acids (volatile fatty acids), alcohols, ammonia and carbon dioxide are the major products of this stage. Production of acids during this period results in a slightly lowered pH, ranging from 5.5 to 6.5 (Ross, 1990). This phase is also known as the acid formation phase.

After several months to a few years the anaerobic phase begins, leading to the production of methane as well as carbon dioxide. This phase, known as methane fermentation (Ross, 1990) or methanogenesis (Farquhar, 1989), results in: (1) a rise in pH to 6.5 to 8, (2) substantial reduction in leachate organic strength, (3) lowered oxidation reduction potential to -330 mV to as low as -450 mV, (Ross, 1990; Bramlett, 1986; Farquhar, 1989). Humic and fulvic organic compounds become more prevalent with increasing landfill age (Lu, 1985). These compounds are strong complexing ligands and, along with pH, can be important in the leaching of heavy metals. Farquhar, Ross, Lu and others present additional information on the "aging" process of landfills.

Figure 10 from Ross (1990) shows this aging process and its different biological phases.

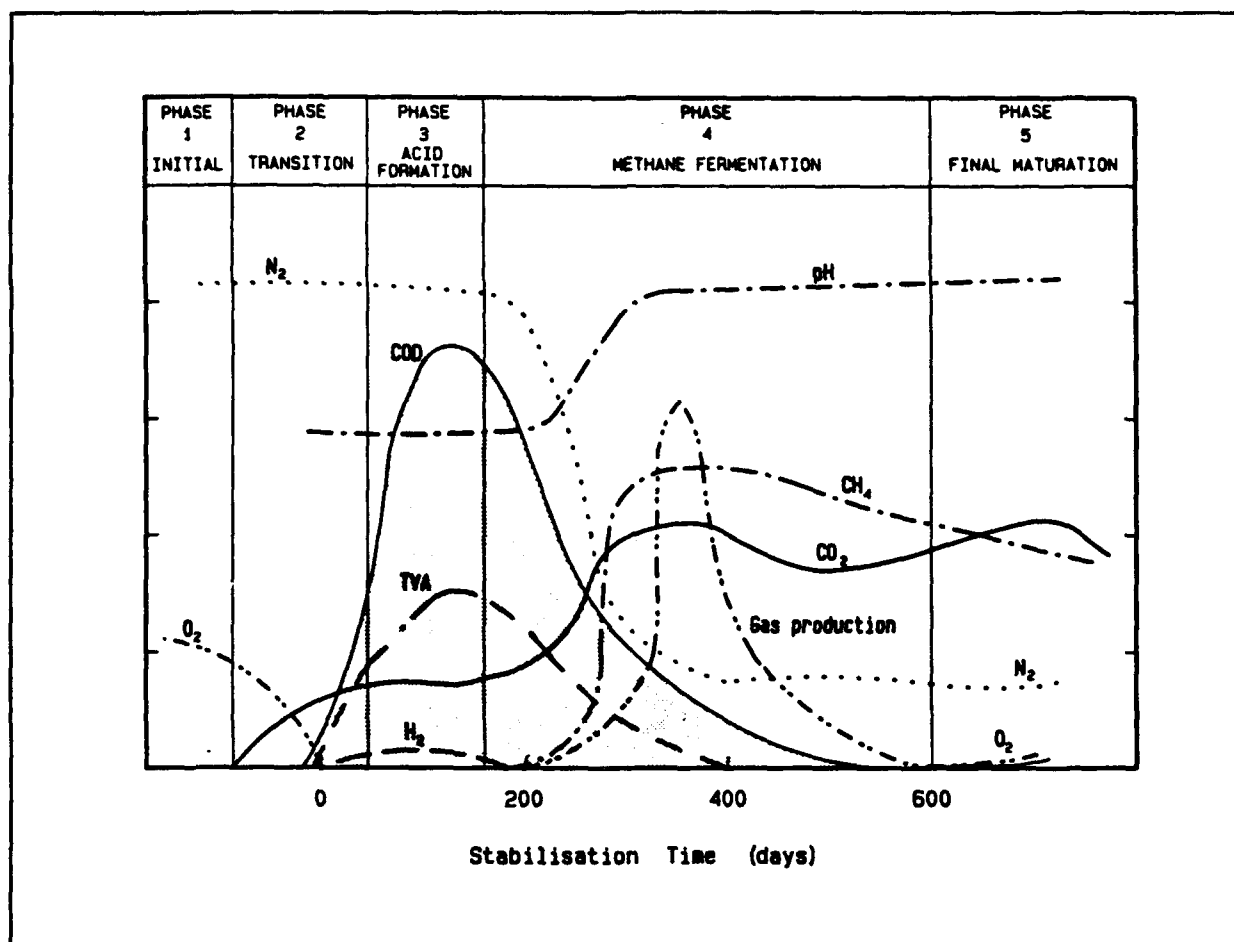


Figure 10. Changes in landfill indicator parameters over time.
Source: Ross, 1990.

Lema, 1988; Farquhar, 1989; Daniel 1984; Harris, 1989; Ross, 1990; McArdle, 1988; and Lu, 1985 all present tables of various leachate compositions. The composition of these leachates is highly variable, however most contain heavy metals, known and suspected hazardous organic substances, pesticides, volatile organics and a host of other constituents including those resistant to biodegradation. Chloride concentrations in the range of 100 to 4,000 mg/L, sulfate levels from 10 to 1,500 mg/L are reported by Lu, 1985. Chloride and sulfate converted to sulfide under

reduced conditions are important because they form precipitates with metals. Burning of wastes, as was done during the early years at Site 7, can result in the oxidation of the sulfur in organic materials in the waste (Nicholson, 1983). Drywall and plaster can also act as a source for sulfate, disposal of this type of waste from construction debris was probably placed in the landfill (Nicholson, 1983). These two sources could result in high sulfate concentrations in leachate from Site 7.

Because of the variability of landfill leachate and the unknown nature of the types and quantities of wastes disposed of at Site 7, the COD of the leachate will be estimated using methods presented by Farquhar (1989) and Lu (1985). Transfer of contaminants from nonaqueous phase liquids (NAPLs) will be estimated using methods of Charbeneau (1993) for LNAPLs and Johnson and Pankow (1992) for DNAPLs.

4.1.3 Hydrogeologic Bio-chemical Reactions

The composition and mobility of leachate in the hydrogeologic system are controlled by biological, geochemical and physical processes (Baedecker, 1979). The physical processes of filtration, mechanical dispersion and dilution are controlled by the porous media, fluid and groundwater flow properties. The biological processes can result in reduction of nitrate to ammonia or nitrogen gas and sulfate to sulfide. These end products, especially sulfide, are important in geochemical reactions which may result in the precipitation of metals. Biological production of carbon dioxide can affect the pH of the water and therefore chemical reactions. Biological processes within the aquifer can also result in the degradation of organic compounds.

Baedecker (1979) discusses three theoretical bio-chemical zones within a landfill leachate contaminated groundwater plume. An aerobic zone is located at the leading edge of the plume where oxygenated water comes into contact with the leachate. In this zone aerobic degradation occurs until no free molecular oxygen exists. Next comes the transition zone where the environment is becoming more reducing (anoxic). Nitrate is reduced to nitrogen gas, then manganese and iron oxides are reduced to lower oxidation states and sulfate is then reduced to sulfide. These reactions occur in an anoxic environment, molecular oxygen is absent and the redox

potential (Eh) is reduced to about -330 mV. Once all sources of free and combined oxygen (electron acceptors) are reduced, anaerobic biological action can take place resulting in fermentation of methane, as organic compounds are utilized as electron acceptors. This is the anaerobic zone and occurs in the "older portions of the plume. Figure 11 (a) shows the corresponding Eh for anaerobic, anoxic and aerobic conditions. Figure 11 (b) shows the Eh level at which some compounds commonly involved in redox reactions are reduced or oxidized.

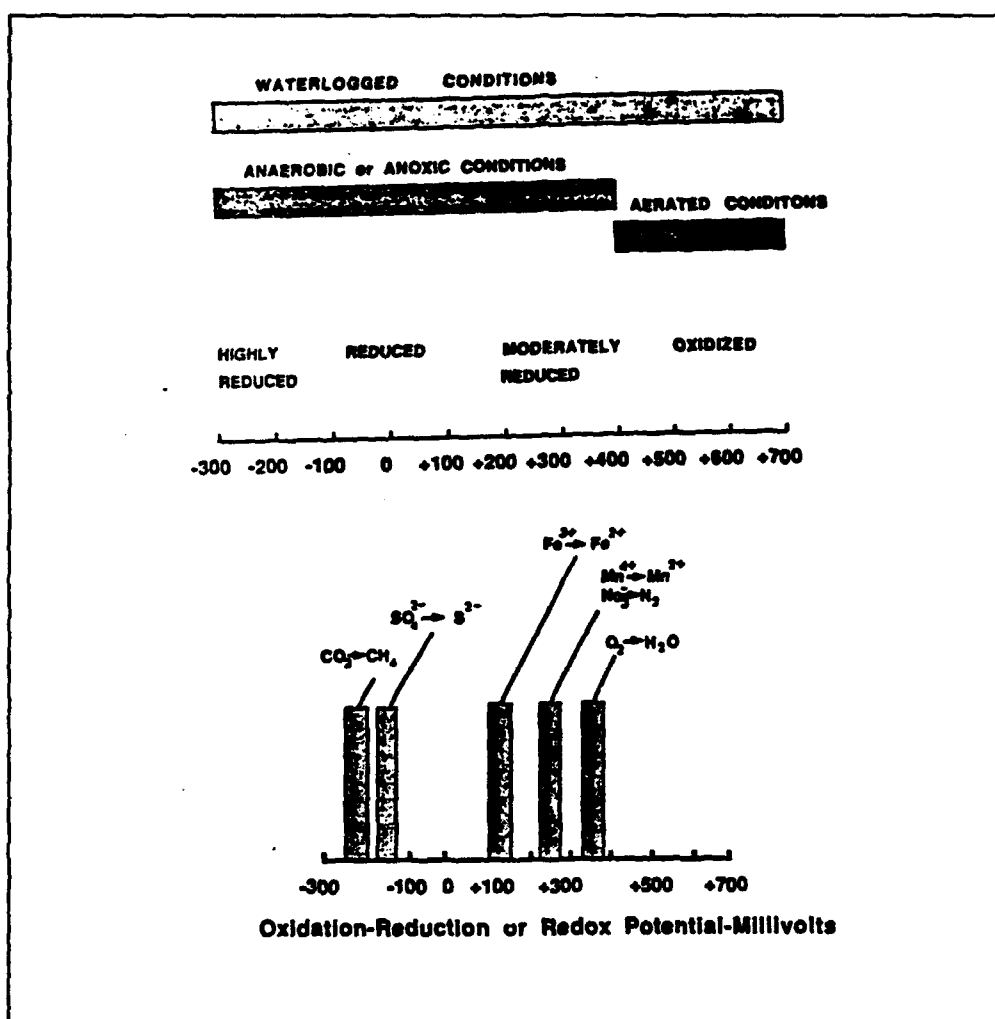


Figure 11. Oxidation-reduction potential, (a) redox potential for various soil conditions, (b) transition redox levels for various compounds. Source: Delaune and Pardue, 1991.

These zones are important because they can result in pH and Eh gradients. Geochemical reactions resulting in precipitation or dissolution can occur along these gradients. pH and Eh are considered controlling variables in the speciation metal compounds. Different species can have very different solubility's as metals may go through several phases such as oxides, sulfides and carbonates as a result of these geochemical zones (Baedecker and Back, 1979). Ion exchange and adsorption processes are surface reactions which can be affected by changes in pH. pH changes can modify the surface electrical charges of the solid particles which participate in these two processes (Freeze, 1979; Williams, 1974)

Most trace metals of environmental significance are influenced by redox conditions. Changes in redox conditions can result in oxidation state changes of the metal or in the nonmetallic constituents with which the metal may form complexes (Freeze and Cherry, 1979). pH versus Eh diagrams can be constructed for waters containing various combining elements or compounds. For a given pH and Eh combination the predominant species can be determined and its solubility will likely control. Freeze and Cherry (1979) present a pH versus pE (similar to Eh) diagram for mercury, this is examined further in section 4.2.1.3.

It should also be noted that metals can form complexes with some organic substances. Humic substances such as humic and fulvic acids, which are typical biodegradation by-products from organic leachates, can act as ligands to form organo-metal complexes (also known as chelates). These bonds may form between functional groups of the humic substances and the metal or between the humic substance and a metal hydroxide colloidal particle (Snoeyink, 1980). Humic acids are soluble in dilute bases but precipitate in dilute acids whereas fulvic acids are soluble in both dilute acids and bases (Snoeyink, 1980). These actions would serve to increase or decrease the amount of a particular metal in solution or suspension. This type of interaction is hard to evaluate but should be considered when determining a retardation factor for the transport of metals (Drever, 1988)

4.1.4 Colloids

Recent work has confirmed the existence of large organic molecules (macromolecules) and colloids in landfill leachate (Gounaris, 1993). This work found significant portions of both organic and inorganic contaminants associated with these colloids. Just as the solid phase of the porous media can sorb organic and inorganic contaminants, so can colloidal and dissolved solids. Colloids are defined as particles with diameters less than 10 μm , which are stable in suspension with water solutions. Gounaris studied a landfill which was operational during the 1960s and 70s. In leachate from this site he found that 7% of the total solids were colloidal, 40% of the hydrophobic organic carbon was partitioned to the colloidal range of particles and 50% of the total iron was colloidal. This last information may be significant because contaminants can be sorbed to these iron oxide colloids or be trapped within due to coprecipitation.

Colloids may be derived from a variety of organic and inorganic materials such as macromolecules from biological activity (either degradation byproducts or microorganisms themselves), microemulsions of NAPLs, chemical precipitates, or clay particles (McCarthy, 1989). The pH, Eh and ionic gradients which can exist in landfill leachate plumes can generate or affect the stability of colloidal suspensions. These effects can be the result of changes to the surface chemistry of the particles, precipitation or dissolution of metals or biological activity.

Hydrophobic organic pollutants, such as PCBs, were found by Gounaris (1993) to be most strongly attached to the 0.1 to 1 μm diameter colloids. Metals (Zn, Pb and Cr) were associated with colloids or complexed with dissolved organic ligands. Dissolved solids are considered those smaller than 1.3 μm . Gounaris states that "whenever stable colloids are present, increased mobilization of metals should be expected". The impact on the mobility of hydrophobic organics contaminants could be more severe. Although Gounaris (1993) found the various colloidal size fractions to have similar partition coefficients between the colloidal organic matter and water, those in the 0.1 to 1 μm fraction were deemed to be the most significant. This is because this size range has a higher mobility, is fairly stable and has high sorptive capacity for the organic contaminants. Colloids larger than 1 μm would be more subject to physical straining

and those smaller than 0.1 μm were not as effective in sorption. (Gounaris, 1993)

Gounaris presents a retardation factor (R) which can be used for organic pollutants in the presence of mobile colloidal organic matter:

$$R = 1 + [K_{ds}/(1 + K_{ocp}C_{ocp})] \times (1 - n)p_s/n$$

Where:

K_{ds} = water/aquifer solids distribution coefficient

$$K_{ds} = K_{ocs} * f$$

f = fraction of organic carbon

K_{ocs} = water/soil organic carbon partition coefficient

K_{ocp} = water/colloidal organic carbon partition coefficient

C_{ocp} = concentration of colloidal Total Organic Carbon (TOC)

n = aquifer porosity

p_s = density of aquifer solids.

Aquifers with low organic carbon content in the porous media would be more susceptible to increased transport via colloids with a high organic carbon content. Gounaris uses the example of an aquifer with $f = 0.001$, $n = 0.3$, $p_s = 2.65$ and $K_{ocp} = K_{ocs}$. Values of C_{ocp} found for the 0.1 to 1 μm fraction were used. His findings show that for this case colloidal transport becomes important for contaminants with $\log K_{oc}$ values greater than 4. For $\log K_{oc} = 5.5$, contaminant velocity with colloids is approximately 10 times that without. For $\log K_{oc}$ values = 6.5 contaminant velocity with colloids is approximately 100 times that without. (Gounaris, 1993)

Although, lack of detailed information regarding the soils and leachate at Site 7 doesn't allow this information to be used to directly compute a retardation factor, it can be used to subjectively select a range of transport modeling inputs and evaluate results. Evaluation of test results for metals when filtered and non-filtered samples are used should also utilize this information. The size of the filter used should be selected to determine mobile versus non-mobile contaminants. This would require information on aquifer pore sizes and colloid properties.

4.1.5 HELP Model Application and Results

The Hydrologic Evaluation of Landfill Performance (HELP) model was used to estimate the amount of leachate produced at this site from precipitation for input to the contaminant transport model. It was also used to evaluate two conceptual cover designs which could be used at Site 7 to minimize infiltration to the waste layer. This model was developed by the US Army Corps of Engineers to allow evaluation of hazardous waste landfill designs by estimating water balance components (run-off, infiltration, evapotranspiration, storage, etc.) and determining the amount percolation through each layer, (Peyton, 1988). Figure 12 illustrates the components of the water balance.

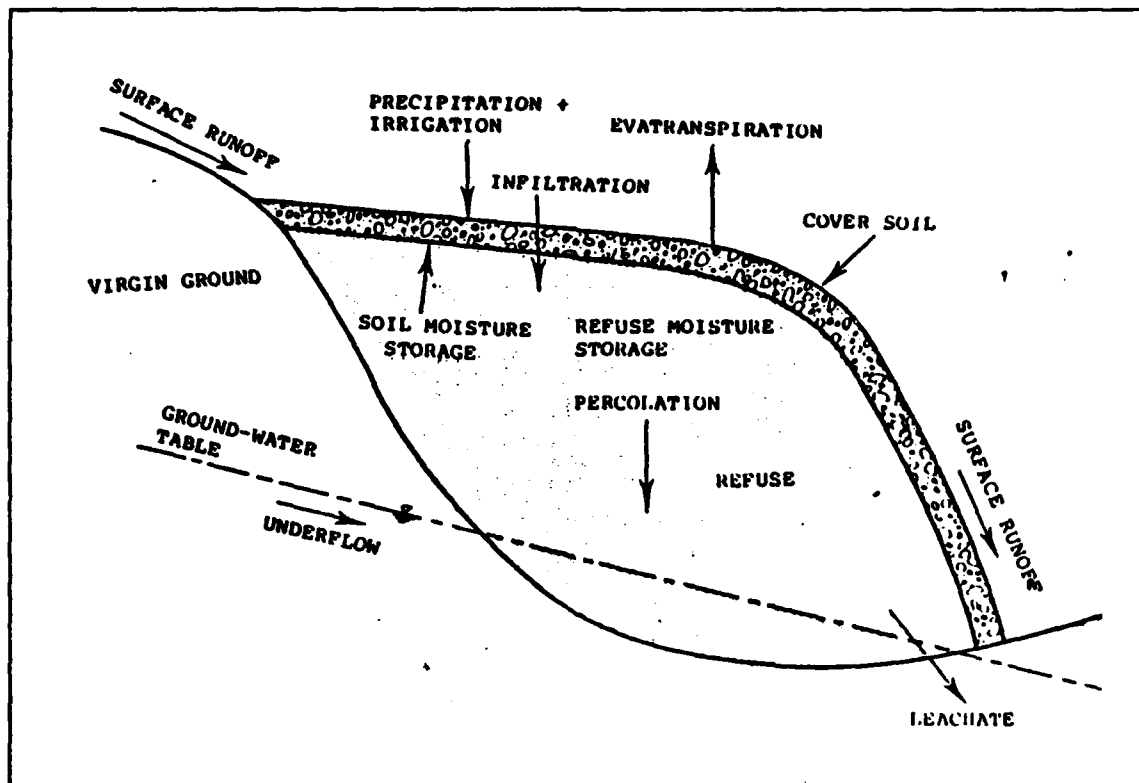


Figure 12. Water balance components. Source: Lu, 1985.

Using a quasi-two dimensional, deterministic methodology, HELP performs a water balance to simulate the hydrologic processes which can result in leachate production. Darcy's law and the principle of continuity are used to route water vertically through soil or waste layers. Lateral flow through lateral drainage layers uses a linearized, steady state approximation (Peyton, 1984). Equations for lateral and vertical flow in a lateral drainage layer are solved simultaneously to divide the flow between that removed from the system and that which continues to flow through a cover or liner (Meeks, 1989).

Precipitation is apportioned between runoff and water available for infiltration using the Soil Conservation Service (SCS) curve number method. Daily surface evaporation is also subtracted from available water to determine infiltration. Evapotranspiration and water stored in soil layers also reduces the amount of water available for leachate production. The computer model includes climatological and growing season data for 102 U. S. cities. Characteristics for several different soils and vegetation types are also available for use. (Schroeder, 1984)

To estimate the amount of leachate produced by the existing landfill, three layers were assumed to exist. The first is 24" of soil which supports vegetative cover, underlain by 72" of waste followed by just 6" of sandy soil above the water table. A SCS curve number of 70 was determined to be appropriate to estimate surface runoff (Lu, 1985). Designating a poor grass cover and a 15" soil evaporation zone recommended for poor grass in Norfolk, (which would both reduce evapotranspiration), a five year average of 11" of percolation reached the water table. With a fair grass cover and a soil evaporation zone of 22", percolation was lowered to 9". Lowering the SCS curve number to 60 (to decrease runoff) and still using fair grass the percolation was 10". During the life of the landfill runoff and vegetative cover would have varied considerably, causing the amount of percolation to change as well. Leachate production of 10"/year will be used for evaluation purposes.

The purpose of a cover is to (1) prevent human or animal contact with hazardous contaminants, (2) prevent off-site migration of surface wastes or contaminants and (3) minimize production of leachate. Two cover designs were evaluated using HELP. The first meets the

minimum requirements for a RCRA hazardous waste landfill (Landreth, 1990). From top to bottom this liner consists of:

- 24" of vegetative cover using natural soils;

- 12" of porous soil for a lateral drainage layer on a minimum 2% slope

- with no more than 200' between drain pipes;

- 24" of compacted clay ($K = 1E-7$ cm/sec);

- 24" of compacted foundation soil; this layer could consist of grading and compacting the existing cover soil and additional fill to allow construction of the clay liner.

The second design is the same as above except a flexible membrane liner (FML) is placed on top of the compacted clay liner (CCL).

The first design (without a FML) allowed approximately 2" of percolation to pass through the landfill. The design with a FML allowed only 0.001" of percolation. The HELP model does not allow selection of a cover system which relies solely on a FML as the barrier layer. As shown by these two designs, the composite action of a CCL overlain by a FML provides better protection than a CCL alone. Any water flowing through a defect in the FML must still flow through the CCL. Also, even with some defects the FML reduces the effective area through which water may pass through the CCL. Common construction practice can reduce defects in an installed FML to an average of 20 holes per hectare (with average size of 0.1 cm^2) and 3 to 5 "small" seam defects per hectare (Daniel, 1993). This provides a substantial reduction in flow area to the CCL and greatly reduces leachate production. Partial output files from HELP for cases with and without a cover are provided in Appendix B.

4.1.6 Chemical Oxygen Demand vs Landfill Age

In the absence of detailed information on particular contaminants in the landfill one alternative is to use the leachate COD concentration as an indicator parameter to model. This has the advantage of being able to use information presented by various investigators as to how leachate COD levels change over time (Lu, 1985) or moisture loading (Farquhar, 1989). As expected, the composition of leachate from any landfill will change over time. Figure 13, taken

from Farquhar (1989), illustrates how the various "ingredients" of the landfill waste will be incorporated into the leachate as a function of their characteristics. If moisture is available, leaching of soluble constituents is readily accomplished. Peak concentrations will be reached in the early months or years. Those wastes which are easily biodegraded will be broken down to more soluble compounds and contribute to leachate composition as shown in Figure 13. Contaminants with low solubility or which are resistant to biological degradation will begin to slowly contribute to leachate composition but persist over a longer period of time.

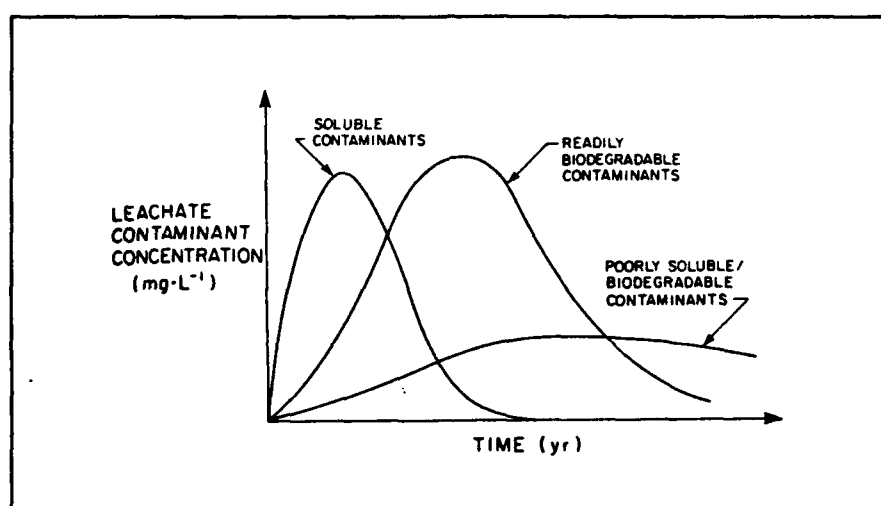


Figure 13. Landfill leachate constituents versus time.
Source: Farquhar, 1989.

Changes in the composition and concentration of leachate organics is a function of the degree of biological decomposition and the amount of water available to remove the soluble products. The amount of water present is also an important factor affecting the rate of biological and chemical decomposition. Along with other factors such as temperature, nutrient availability, time for reactions to occur and the absence of toxic substances, water is a required input into the biological decomposition process. Several studies using lysimeters, field or laboratory test cells or actual landfills have looked at the relationship between leachate composition and the time which has passed since placement of the waste.

Lu (1985) compiled data from a number of studies in an effort to develop a relationship between landfill age and municipal solid waste leachate composition. For many of the leachate constituents, including COD, a first order rate equation was developed which served as an upper bound on the available data. Figure 14 shows the data and upper bound curve for COD. The equation for the upper bound curve was used to develop a COD production schedule for Site 7. Although specific information regarding development of the landfill at Site 7 is not known, it is believed that it began at the eastern edge and developed westward. In an effort to model the landfill, it was broken into six north-south "strips" or cells. Each strip is assumed to have received waste for one-sixth of the period the landfill was open. This amounts to approximately three years per cell (1034 days or 2.83 years). Using Lu's upper bound COD production equation, COD concentrations for each landfill cell was determined for periods of time from 1962 when landfill operations began, Table 3. Although, early landfill operations included open burning, no attempt is made to incorporate this into the COD estimates.

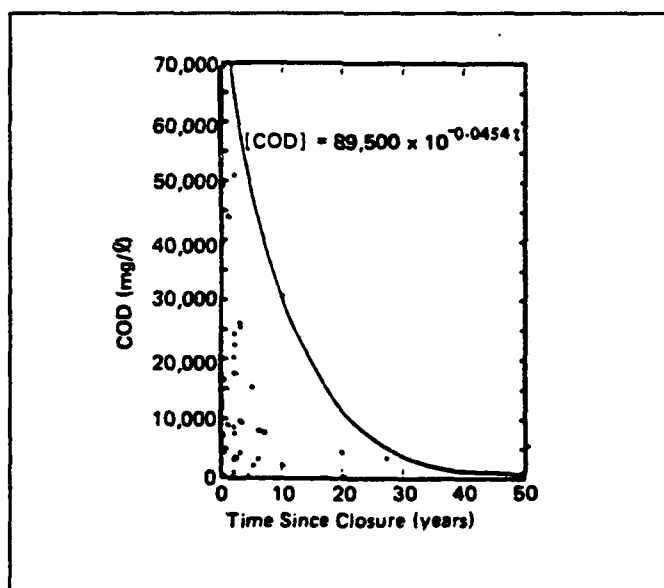


Figure 14. Leachate COD concentration vs time.
Source: Lu, 1985.

Years of Cell Ops	Yrs since closure of cell 1	COD Conc. (mg/L)	Yrs since closure of cell 2	COD Conc. (mg/L)	Yrs since closure of cell 3	COD Conc. (mg/L)	Yrs since closure of cell 4	COD Conc. (mg/L)	Yrs since closure of cell 5	COD Conc. (mg/L)	Yrs since closure of cell 6	COD Conc. (mg/L)
1962	0	89500	----	----	----	----	----	----	----	----	----	----
1966	1.5	74511	0	89500	----	----	----	----	----	----	----	----
1968	4.5	55914	1.5	74511	0	89500	----	----	----	----	----	----
1971	7	43056	4	58915	1	80416	0	89500	----	----	----	----
1973	9.5	33153	6.5	45345	3.5	62076	1.5	74511	0	89500	----	----
1976	12.5	24228	9.5	33153	6.5	45345	4.5	55914	1.5	74511	0	89500
1979	17.5	14346	14.5	19657	11.5	26898	9.5	33153	6.5	45345	3.5	62076
1986	23	8084	20	11042	17	15136	15	18456	12	25528	9	34932
1990	26.5	5607	23.5	7677	20.5	10498	18.5	12940	15.5	17706	12.5	24228
1993												
NOTES:												
COD concentrations determined using $COD = 89,500 \times 10^{-4} (0.0454 \times t)$ where t is time since cell closure in years.												
The landfill was broken into arbitrary "cells of operation" for modeling purposes. It is believed that development of the landfill was from east to west. So the landfill was divided into 6 longitudinal cells. To determine COD concentration the midpoint age of the cell since closure of that cell was used.												

Table 3. Landfill leachate COD production schedule.

Farquhar (1989) uses work done which relates leachate constituent concentrations to the amount of moisture added to municipal solid waste. The results are leachate constituent production curves which relate the moisture loading (in liters of water per kg of dry refuse) to either leachate constituent concentration or to the cumulative amount of a contaminant leached. Figure 15 shows the leachate COD production curve with an upper bound curve added. Both this information and that of Lu is based on municipal solid waste (MSW) and not mixed industrial waste and MSW as placed in the landfill at Site 7, because of this the upper bound will be used as an estimate of the leachate COD from this site.

Using 10" of leachate production per year, from HELP, and assuming a waste depth of six feet with a density of 750 lbs/yds at a 20% moisture content (Tchbanoglous, 1977) the moisture loading at Site 7 would be approximately 0.25 L/kg/year. A COD production schedule, based on the cumulative moisture loading to the six landfill cells and the upper bound curve in Figure 15 for COD concentration, is presented in Table 4. The COD concentrations found by this second method are somewhat lower than those using Lu's information. This method seems more rational as differences in arid versus wet regions would be accounted for by moisture loading. Results

from the Farquhar method will be used in the groundwater contaminant transport modeling in Section 6.

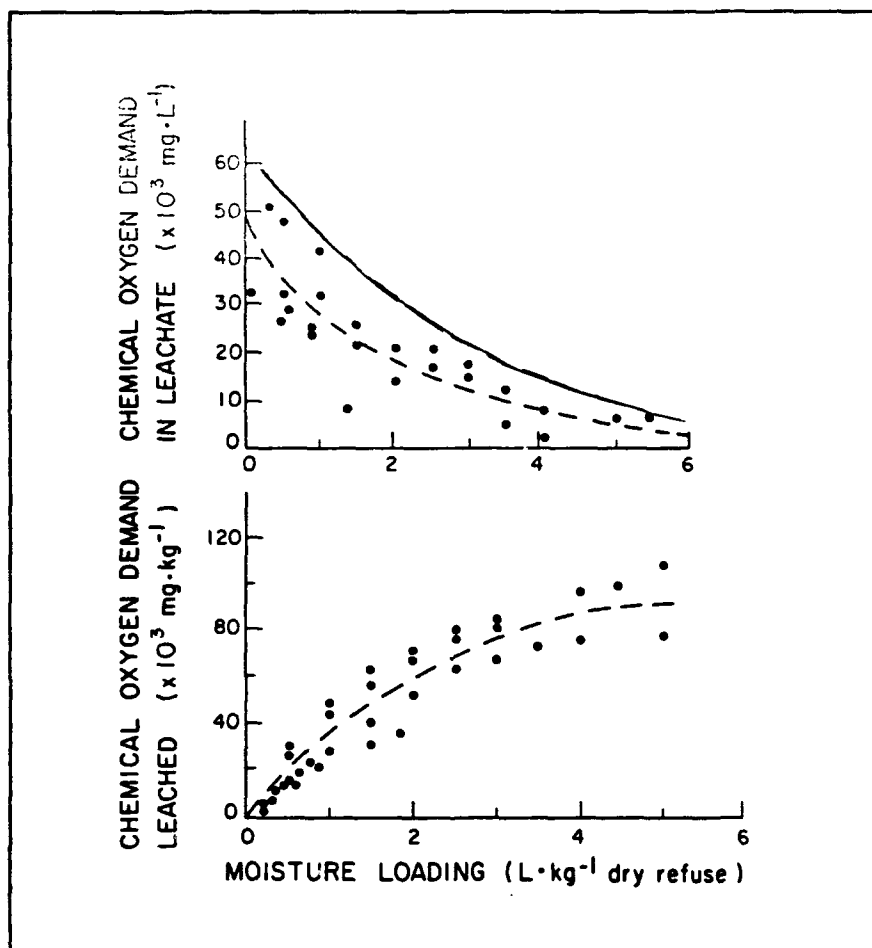


Figure 15. Leachate COD concentration vs moisture loading.
Source: Farquhar, 1989.

Years of Cell Ops	Cumulative Moisture Loading Per Cell 1 5,000,000	COD conc. from Cell 1	Ave COD from Cell 1	Cumulative Moisture Loading Per Cell 2 5,000,000	Ave COD from Cell 2	Cumulative Moisture Loading Per Cell 3 5,000,000	Ave COD from Cell 3	Cumulative Moisture Loading Per Cell 4 5,000,000	Ave COD from Cell 4	Cumulative Moisture Loading Per Cell 5 5,000,000	Ave COD from Cell 5	Cumulative Moisture Loading Per Cell 6 5,000,000	Ave COD from Cell 6
1962		80,000	67500		0		0		0		0		0
1965	0.75	55,000	47500	0	67500	0	0	0	0	0	0	0	0
1968	1.5	40,000		0.75		0		0		0		0	
1971	2.25	32000	36000	1.5	47500	0.75	67500	0	0	0	0	0	0
1973	2.75	28000	30000	2	40000	1.25	50000	0.5	70000	0	0	0	0
1976	3.5	20000	24000	2.75	32000	2	42000	1.25	54000	0.75	67500	0	0
1979	4.25	18000	19000	3.5	21000	2.75	28000	2	42000	1.5	47500	0.75	67500
1986	6	10000	14000	5.25	17000	4.5	20000	3.75	24000	3.25	28000	2.5	40000
1990	7	7000	8500	6.25	10000	5.5	13000	4.75	15000	4.25	19000	3.5	23000
1993	7.75	6000	6500	7	8500	6.25	9000	5.5	11000	5	14000	4.25	19000
NOTES:													
COD concentrations determined using leachate production curve modified from Farquhar, 1989.													
Leachate production curve gives COD vs moisture loading. L moisture per kg dry waste.													
The landfill was broken into arbitrary 'cells of operation' for modeling purposes.													
It is believed that development of the landfill was from east to west. So the landfill was divided into 6 longitudinal cells. To determine COD concentration the midpoint age of the cell since closure of that cell was used.													
Annual moisture loading is 0.25 L per kg dry waste per year (10 inches per square ft per year).													

Table 4. Landfill leachate COD production schedule, Farquhar.

4.2 Inorganics

Leachate produced as water percolates through layers of waste in a landfill can contain large amounts of inorganic contaminants. Freeze (1979), Lu (1985) and Daniel (1984) present information on the types and concentrations of inorganics which can be found in leachate from MSW landfills. Some of this data incorporates data from landfills which were in use or even closed prior to passage of the Resource Conservation and Recovery Act (RCRA) and therefore likely contain a variety of industrial wastes along with the MSW.

Because of the complex chemical and biological reactions which can occur to and between substances in landfills the composition of leachate for any particular site is difficult to predict. Table 5, taken from Freeze (1979), Lu (1985) and Daniel (1984) lists some inorganic constituents which are likely to be found in landfill leachate and typical concentration ranges.

Chloride and sulfate concentrations are important when considering heavy metals. Chloride and sulfide, reduced from sulfate, can combine with trace metals to form compounds with varying solubility's. Landfill leachates often contain high concentrations of toxic heavy metals, which when present in even small concentrations can have adverse impacts on both plants and animals (Bolton, 1991). These metals can form complexes with inorganic ligands (sulfate, sulfide, chloride, carbonates, fluorine, nitrate and hydroxides) and organic macromolecules such as humic substances (Leckie, 1974). Solution pH, redox potential (Eh), ionic strength, and concentration of organic and inorganic ligands in solution play a large role in determining the form of metals in solution. Some of these complexes are highly insoluble whereas others are readily soluble. Therefore, what form the metals are in, impacts the mobility of these contaminants. The toxicity of metals can also vary according to what form they are in (Moore, 1984).

Table 5 Typical Landfill Leachate Constituent Concentrations

Constituent	Concentration range (mg/L)
K ⁺	200-3, 500 (1, 2)
Na ⁺	200-1, 200 (1, 2)
Ca ²⁺	100-3, 000 (1)
Mg ⁺	100-1, 500 (1)
Cl ⁻	300-4, 000 (1, 2)
SO ₄ ²⁻	10-1, 500 (1, 2)
Alkalinity	500-20, 000 (1, 2)
Fe (total)	1-1, 000 (1, 2)
Mn	0.1-100 (1)
Cu	< 10 (1)
Ni	0.1-1 (1)
Zn	0.1-100 (1)
Pb	< 5 (1)
Hg	0.001-0.16 (2, 3)
As	0.0-11.6 (3)
Se	0.08-0.16 (1,2)
B	5.0-8.4 (3)
Cr	0.01-10 (2)
Cd	0.001-0.5 (2, 3)
NO ₃ ⁻	0.1-10 (1)
NH ₄ ⁺	10-10, 000 (1)
P as PO ₄	1-100 (1, 2)
Organic N	10-1000 (1)
Total DOC*	200-30, 000 (1, 2)
COD	1, 000-90, 000 (1)
Total dissolved solids (TDS)	5, 000-40, 000 (1)
pH	4-9 (1, 2)
Redox potential (mV)	-450 to +160 (3)

* DOC = Dissolved organic carbon.

(1) Freeze, 1979

(2) Lu, 1985

(3) Daniel, 1984

Transport of heavy metals in porous media, excluding diffusion, requires that the metal is solubilized in aqueous solution or is associated with mobile particulate matter such as colloids. In porous media heavy metals can be present: (1) on ion exchange sites of the porous media or colloidal solids, (2) be sorbed on, coprecipitated with or complexed with other inorganics, (3) be sorbed on or complexed with organic substances (Dowdy, 1983). Most metals are more soluble in low pH solutions. The redox condition of the water affects the oxidation state of the metal and the non-metal ligands, thereby affecting what reactions occur. pH and Eh can also change the sorption and ion exchange properties of the porous media and colloidal solids (Freeze and Cherry, 1979).

The concentration of other inorganic ions present can impact the solubility of some metal complexes, for instance, as chloride concentration increases the solubility of manganese increases (Leckie, 1974). Metal hydroxides and coprecipitated hydroxides and clay minerals typically have a higher cation exchange capability in basic solutions. This can cause strong binding of hydrolyzable metal ions to the surfaces of these particles (Williams, 1974). These "receiving" particles may be a stationary part of the porous media or may be mobile colloids.

pH vs Eh diagrams can be developed for particular solutions to determine which compounds of a metal will predominate at different pH-Eh situations. These diagrams are useful in interpreting conditions under which heavy metals are mobile. As described earlier, groundwater contaminated by leachate from a landfill will typically undergo a transition from a condition where the water is oxidizing (positive Eh due to the presence of free oxygen) to a reducing environment (negative Eh) because of the biological decomposition of organic substances. Three zones were defined by Baedecker (1979): aerobic, transition and anaerobic. Changes in the composition of metal complexes can occur as the water passes through these zones. The pH and Eh changes from zone to zone as can the oxidation state of inorganic substances. For instance sulfate becomes sulfide as the water becomes anaerobic. Sulfide can form highly insoluble complexes with most heavy metals under these conditions (Stumm and

Morgan, 1981).

Metal complexation (or chelation) with organic ligands and sorption to colloidal materials can increase the "mobile" concentration of a heavy metal. Many of these organic ligands are present in landfill leachate in the form of humic substances. Because of the large molecular size of these organic ligands they have the ability to combine with a considerable quantity of metal ions (Snoeyink, 1980). Two modes of bonding between the organics and metals are significant: (1) bonds between functional groups on the humic substance and the metal to form a complex, and (2) sorption of a metal hydroxide to the surface of the humic substance (humic and fulvic acids), (Snoeyink, 1980). Within the pH expected in the leachate and groundwater solution (5.5 to 8) these substances are soluble and may transport metals through the porous media.

The landfill at Site 7 is probably underlain by anaerobic groundwater. Pockets of aerobic conditions may exist in small areas which received no wastes or perhaps no biodegradable material remains. Groundwater flowing in from upgradient may be aerobic or at least anoxic. The monitoring wells nearest the cove had higher chloride concentrations (0.3M) versus the upgradient wells (0.004M); reported sulfate concentrations also increased near the cove, from 0.003M to 0.01M (Ebasco, 1991). Sulfide would be reported as sulfate if samples were allowed to aerate prior to analysis. All this combines to provide Eh and pH gradients as well as a chloride and sulfide (or sulfate) concentration gradients. To evaluate the effects on metals under these conditions, pH-Eh diagrams can be used for mercury under different conditions.

Mercury was chosen to illustrate the impact of geochemistry on the mobility of heavy metals at this site, because of recent concern over surface water and surface sediment mercury levels, which may be derived from groundwater transported mercury. Metals speciation can also be predicted using chemical equilibrium models like MINTEQ (Metal Speciation Equilibrium Model for Surface and Ground Water), a computer program developed by the EPA.

4.2.1 Mercury

Mercury is a silver white metal which is liquid at room temperature, its melting point and boiling point are approximately -39°C and 357°C, respectively. In the elemental form it is highly

insoluble in water and has a specific gravity of 13.546 and vapor pressure of 0.0012 mm Hg, both reported at 20°C. Mercury can exist in three oxidation states: elemental, mercurous (+1) and mercuric (+2). Several forms of both inorganic and organic mercury compounds or complexes can be found in the aqueous environment. These compounds have considerably different properties with regards to solubility, sorption and toxicity. Mercury has the lowest Maximum Contaminant Level (MCL) set by the Safe Drinking Water Act (SDWA). (EPA, 1980; Moore, 1984; Fetter, 1992)

Several investigators discuss the ability of certain commonly found microorganisms to convert inorganic and organic forms of mercury into the more toxic methyl or dimethyl mercury. These two methylated forms of mercury are more soluble in water and they are also more biologically active than other forms. While the toxicity of mercury in its various forms is discussed by several authors, of interest to note is that mercury, unlike most other pollutants, mercury has direct toxic effects on aquatic life at about the same concentrations that it affects the uses of aquatic life (food chain) through bioaccumulation. (EPA, 1980; Moore, 1984; Forsner, 1981)

Using toxicity characteristics mercury can be grouped into three categories: (1) forms of mercury in the elemental form (zero oxidation state), present as metallic mercury or mercury vapor; (2) inorganic compounds of mercury, which includes salts of the two oxidation states (Hg_2^{++} and Hg^{++}); and (3) organic mercury compounds, in which mercury is covalently bonded to at least one carbon atom. This third category is the most important one according to toxicity. Toxic properties of this group vary widely, with the most important sub-category being the methyl mercury and short-chain mercurial compounds. Methyl mercury is quickly taken up by aquatic life, with demethylation being a very slow process. Due to slow transformation into methyl mercury and its rapid uptake by aquatic life, methyl mercury has usually been found to make-up less than 1 to 5% of the total mercury present. (EPA, 1980; Moore, 1984)

4.2.1.1 Sources

Several properties of mercury make it useful for a variety of industrial and commercial applications. Liquidity at room temperature, uniform volume expansion/contraction over a large

temperature span, high surface tension, its non-wetting quality with respect to glass and its high density provide the basis for its use in temperature and pressure measuring instruments. Low electrical resistance and high thermal conductivity make it useful as an electrical conductor and coolant in a variety of electrical instruments and equipment. Organic mercury compounds have found wide spread use as insecticides, fungicides, bactericides and pharmaceuticals, including mildew resistant paints. Mercury amalgams are used in dental applications and mercury oxides, sulfides and chlorides are used as catalysts in a variety manufacturing processes. (Moore, 1984; Forstner, 1981; EPA, 1980) Because mercury has been widely incorporated into many manufactured instruments and products and its widespread industrial use means it also ends up in landfills. Reported landfill leachate mercury concentrations as shown in Table 5 vary from 0.001 to 0.2 mg/L (Lu, 1985; Freeze, 1979).

Atmospheric fallout from fossil fuel power plants and industrial processes provide regional mercury background pollutant levels. Municipal sewage outfalls have also been found to be sources of mercury to the aquatic environment. In numerous studies of North American Atlantic and Gulf Coast regions there was a high correlation of high mercury concentrations in receiving waters to municipal or industrial sewer outfalls. The mercury was predominantly found in the silt and clay soil fractions which had high organic content. (Forstner, 1981) The Hampton Roads Sanitation District has a sewage treatment plant just across Amphibious Drive from the landfill at Site 7, the location of past discharge and overflow outlets should be determined as a possible source of mercury.

4.2.1.2 Speciation

Mercury in aqueous environments can exist in any of its three oxidation states; either as elemental mercury or in the +1 or +2 oxidation states combined with various other substances. The characteristics of the species and its distribution between solid or dissolved phases will depend in part on the pH, Eh and the types and concentrations of anions and ligands present. In aerobic waters with Eh > 500 mV the mercuric species (+2) will predominate. Under reduced conditions the elemental species will be favored. However the presence of sulfide complexes can

combine with Hg^{++} to stabilize it even at low redox potentials. (Moore, 1984; Freeze, 1979; Stumm and Morgan, 1981)

Association with Inorganic Ligands: Metals ions in solution can bond covalently or electrostatically with a variety of inorganic ligands to form compounds or complexed ions. Mercuric ions (Hg^{++}) can form strong covalent bonds with sulfide and chloride ions. Which ion is bonded with is predominately controlled by the redox potential; sulfide at lower Eh and chloride at higher Eh (Freeze, 1979). The mercuric ion can also hydrolyze, forming $\text{Hg}(\text{OH})_2$. The hydrolyzed form grows in predominance as the pH increases and sulfide and chloride concentrations decrease. Leckie (1974) and Forstner (1981) present solubility and complex formation equilibria for various compounds of mercury and chloride, sulfide or hydroxide. As with chloride, bromide (Br^-) and iodide (I^-) ions can also combine with mercuric ions, in the order of complex bond strength of $\text{Cl}^- > \text{Br}^- > \text{I}^-$ (Leckie, 1974).

pH-Eh diagrams can be developed for specific solutions showing which compounds will be stable in various pH-Eh regions. These diagrams are developed utilizing the chemical thermodynamics of the various reactions under consideration and with the assumption that the oxidation-reduction reactions have reached equilibrium. After determining the prevalent species at a given pH-Eh, the concentration expected in aqueous form can be found from the solubility of that form. (Stumm and Morgan, 1981; Moore, 1984; US EPA, 1980; Leckie, 1974; Fetter, 1993)

Association with Organic Ligands: Mercury can also form stable complexes with a variety of organic ligands such as proteins, amino acids, humic substances and microorganisms. Sulfur containing organic substances can form strong covalent bonds with mercury. There has been some correlation found between the molecular weight and carbon content of the organic compounds and the degree of mercury associated with the various molecular weight fractions (Moore, 1984). The stability of these complexes varies with pH and salinity (Williams, 1974). Humic and fulvic acids are the result of biodegradation of organic substances within the landfill and are two the more important organic ligands found in leachate from landfills. As pH and

salinity increase these substances tend to flocculate and settle out of solution (Williams, 1974).

Some of these organic ligands are associated with the dissolved solids fraction which can bind and transport considerable amounts of mercury. The concentration of the organic ligands in a polluted water is usually much higher than the concentration of metals which may be competing to form with these ligands. This allows the trace metals to be considered individually in this case (Moore, 1984).

Methylation of mercury can be accomplished by biological or chemical reactions. Free mercuric ions (Hg^{++}) must be present, along with methyl donor molecules for methylation to occur (Moore, 1984). Stumm and Morgan (1981) present information on the stability of methyl mercury and its complexes.

Association with Solids: Mercury can associate with solid particles of the porous media as well as with a variety of suspended solid particles which are found in natural and polluted waters. The degree and strength of this association is controlled by the nature of the particulates and solution water parameters such as pH, Eh, salinity, and the presence and concentration of other ligands (Moore, 1984).

Mercury as with other trace metals can be held onto silica particles like quartz (SiO_2) through adsorption or ion exchange forces (Leckie, 1974). This association with silica is highly dependent upon pH due to the effects of pH changes on the level of surface charges on the solid particles. For most trace metals, there can be a critical pH range over which the percent adsorbed changes from negligible to a maximum amount, perhaps approaching 100%. For mercury this relationship is also affected by the chloride concentration. As the chloride concentration increases, the critical pH range increases. As shown by Leckie (1974), Figure 16, the pH range where the percent adsorbed jumps from near zero to near 60% increases from a range of about 6 to 7.5 when $[\text{Cl}^-] = 10^{-3} \text{ M}$ to a pH range of 8 to 9.5 where the percent adsorbed makes a similar jump (from 0 to 60%) when $[\text{Cl}^-] = 10^{-1} \text{ M}$. The pH where the percent adsorbed jumps coincides with the pH where $\text{Hg}(\text{OH})_2^0$ becomes the predominate species over $\text{Hg}^{++} - \text{Cl}^-$ complexes. This indicates the chloride complexes are only weakly adsorbed whereas the

hydroxide complexes are more strongly adsorbed. (Leckie, 1974)

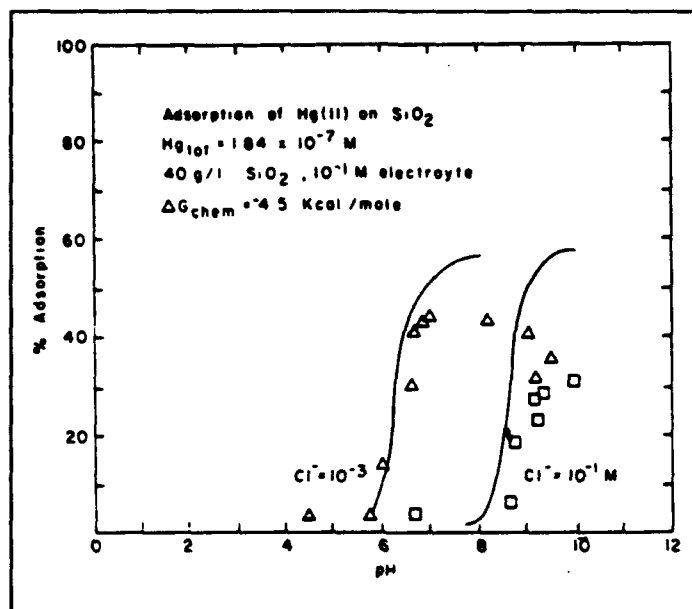


Figure 16. Experimental adsorption isotherm for Hg(II) on quartz with respect to pH and chloride strength. Ionic strength is 1×10^{-1} . Source: Leckie, 1974.

This jump in chloride concentration is similar to the change in chloride concentration found as the water flowing under the landfill at Site 7 experiences as it changes from its background levels ($\sim 0.004M$) to $\sim 0.3M$ as the water reaches a zone near the cove which has a high chloride content from the hydraulic connection with the cove (Ebasco, 1991). With reported pHs in this area (5.5 to 6.5) this indicates that adsorption of mercury hydroxides may occur upgradient from this higher chloride zone but not within it.

Mercury may also be sorbed or complexed to the organic matter found within the porous media or to colloidal organic matter. This association would be subject to the same controls as discussed above on the section on association with organic ligands. Mercury sorption to sediments has been correlated to surface area > organic content > cation exchange capacity > grain size (Moore, 1984). These properties indicate that clays and organic soils (or the organic content of the soils) favor higher sorption capacity versus clean sandy soils.

Mercury and other trace metals can also be coprecipitated with iron, manganese and other metals oxides and carbonates or sulfur- metal compounds. Leaching of mercury from sediments has been observed in solutions of NaCl and surfactants derived from commercial detergents (Moore, 1984). Surfactants can be strong complexing agents and these associations between mercury and solids should be evaluated in the context of the mobility of the solids.

4.2.1.3 pH vs Eh Diagrams

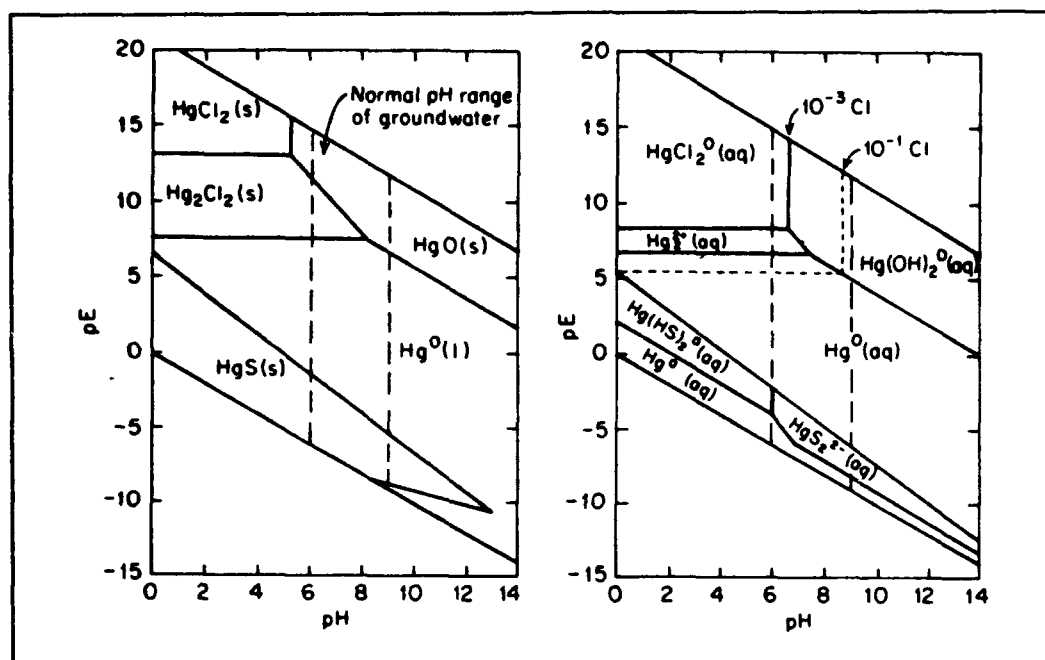


Figure 17. Stability fields of solid and aqueous species of Hg as functions of pH and pE. (a) Solid phases with 10^{-3} molal Cl^- and SO_4^{2-} . (b) Aqueous species with 10^{-3} M SO_4^{2-} and 10^{-3} M and 10^{-1} M Cl^- .

The pH-pE diagrams for mercury in solution with chloride and sulfide presented by Freeze and Cherry (1979) can be used along with an EPA developed geochemical computer model to determine the form of mercury within the landfill leachate and changes that can occur as the leachate travels through the groundwater. The program used is the Metal Speciation Equilibrium

Model for Surface and Groundwater (MINTEQA, version A2). As its title suggests this program determines the speciation of metals within aqueous solutions. The pH, Eh (or pE), ionic strength and various substances with their concentrations are provided as input and the equilibrium speciation for those conditions is computed.

Figure 17, taken from Freeze and Cherry, is developed for chloride concentrations of 10^{-1} and 10^{-3} molal with a sulfate concentration of 10^{-3} molal. These are similar to the concentrations at Site 7 (Ebasco, 1991), molarity and molality at low concentrations such as these are nearly equivalent. pE is the negative logarithm of the electron concentration, analogous to pH but for proton concentrations. Eh is the redox potential and is equal to the energy gained in the transfer of one mole of electrons from an oxidant to H_2 (Freeze and Cherry, 1979). pE and Eh are related by the following equation:

$$pE = (nF/2.3RT)Eh$$

where: $pE = -\log(e)$,

Eh = redox potential (volts),

n = number of electrons transferred in the half
reaction of the oxidation-reduction reaction,

F = Faraday constant (9.65×10^4 C/mol),

R = universal gas constant (8.314 J/K mol),

T = absolute temperature ($C + 273.15 = K$).

For a reaction where $n = 1$ and $20^\circ C$, this equation becomes:

$$pE = 17.2 Eh$$

Given a pH range of 5.5 to 7.5 and pE range of -3.4 to -1.0 from the monitoring wells at Site 7, (CH2M Hill, 1986). Figure 17 indicates that the expected forms of precipitated mercury are $HgS(s)$ or $Hg(l)$ with aqueous species of Hg^0 , $Hg(HS)_2$ or HgS_2^{2-} . Given below are solubility constants for several mercury compounds.

Table 6 Solubility Equilibria for Mercury

<u>Equation</u>	<u>log K(25°C)</u>
$\text{HgS(s)} = \text{Hg}^{+2} + \text{S}^{2-}$	-52.4 (2,3)
$\text{Hg(l)} = \text{Hg (aq)}$	-6.5 (1)
$\text{HgO(s)} + \text{H}_2\text{O} = \text{Hg(OH)(aq)}$	-3.7 (1)
$\text{HgO(s)} + \text{H}_2\text{O} = \text{Hg}^{2+} + 2\text{OH}$	-25.7 (1,2)
$\text{HgCl}_2\text{(s)} = \text{Hg}^{2+} + 2\text{Cl}^-$	-13.8 (1)
$\text{Hg}_2\text{Cl}_2\text{(s)} = \text{Hg}_2^{2+} + 2\text{Cl}^-$	-18.0 (1)

(1) Leckie, 1974

(2) Forstner, 1981

(3) Stumm and Morgan, 1981

First MINTEQ was used to try and reproduce the results of Figure 17 by using the same sulfide and chloride concentrations and varying pH and pE. The results were comparable, for instance with pE = +10 and pH = 6 the results indicated that calomel (Hg_2Cl_2) was the dominant solid species. MINTEQ was then run using the values shown in Table 7 to simulate the geochemical changes that occur as the groundwater nears the cove and changes to pH and pE which could occur over time. The pH and pE values were chosen from current values and then those that are expected as the landfill ages farther, i.e., increasing pH and pE as the leachate becomes less acidic and less reduced.

Using the values in Table 7, MINTEQ was run eight times, one set of four for near the cove and one set of four for upgradient. The four runs from each set provided the speciation at pH = 5.5 at pE = -3.4 and +3.4, similarly for pH = 7.5. In all cases, MINTEQ indicated that $\text{Hg}^0\text{(l)}$ would be the predominant precipitated species. Some other solid species were present in small amounts, for instance, the log saturation index for calomel (Hg_2Cl_2) varied from -4 near the cove to -7.5 away from the cove. The saturation index is the reaction quotient divided by the solubility constant ($S_i = Q/K_{eq}$), resulting in a calomel concentration of approximately 10^{-22}M . A partial listing from a MINTEQ file is provided in Appendix C.

Table 7 MINTEQ Input Parameters

<u>Substance</u>	<u>Conc. near cove [M]</u>	<u>Conc. upgradient [M]</u>
Cl ⁻	0.3	0.004
Hg ₂ ²⁺	0.00005	0.00005
Na ⁺	0.3	0.004
Ca ²⁺	0.1	0.001
CO ₃ ²⁻	0.1	0.001
HS ⁻	0.1	0.003
pH	5.5/7.5	5.5/7.5
pE	-3.4/+3.4	-3.4/+3.4
Ionic strength	0.53	0.03
Temperature	20°C	20°C

Source: Ebasco, 1991 and CH2M Hill, 1986

The aqueous species produced by Hg(l), as indicated by Figure 17, is the zero oxidation state (elemental) Hg⁰(aq), which has a log K_{eq} = -6.5 at 25°C. This would result in a maximum aqueous phase concentration of 110 µg/L ($10^{-6.5} \times 200 \text{ g/mol} \times 10^6 \mu\text{g/L}$). The aqueous phase concentration could not exceed this amount due to solubility limits, but the actual concentration would be controlled by the amount of mercury present. In this non-ionic form the Hg⁰ (l and aq) would be less susceptible to methylation (Moore, 1984) and less likely to be sorbed or complexed due to a lack of charge. This would increase the mobility of the mercury. In addition to increased aqueous phase mobility, Stumm and Morgan (1981) note that the volatility of Hg⁰(aq) is relatively large as indicated by its Henry's Law constant ($P_{\text{Hg}} = 8.5 \text{ atm/M}$) and that the un-ionized mercury in solution could be readily lost through vaporization. In this case it would be free to be transported through by the soil gas phase.

4.2.1.4 Discussion

This section has raised a lot of questions regarding the possible mobility of mercury but has not necessarily answered any. It appears that the mercury would be quite mobile in both the groundwater as well as the soil vapor. One question left unanswered is whether transport through

the soil vapor phase or groundwater could result in the mercury concentration found in the drainage canal sediments and water. Perhaps a more likely source for this mercury is overland transport via rainfall runoff or blowing dust. Either mechanism could move mercury from the surface soils attached to soil or other particulates resulting from the mixing that occurred when the landfill was in operation and subsequent grading.

5.0 Non-Aqueous Phase Liquids (NAPLs)

Non-aqueous phase liquids are immiscible with water and have low to very low solubility levels in water (several thousands of mg/L to tens of mg/L). These liquids may be present in aquifers and the unsaturated zone as a separate phase (free liquid), dissolved phase, vapor phase (unsaturated zone) or sorbed to porous media solids or colloidal solids. NAPL densities may be less or greater than that of water, i.e., light NAPLs (LNAPLs) or dense NAPLs (DNAPLs). Typical LNAPLs encountered include gasoline and other petroleum hydrocarbon products (floaters). Chlorinated hydrocarbons such as the many solvents are DNAPLs (sinkers). NAPLs can become trapped in the porous media and then act as a long term source for groundwater contamination due to their low solubility's.

Many of the wastes disposed of at Site 7 are LNAPLs or DNAPLs, see Table 2. The category of oils, lubricants, degreasers and solvent probably includes both. Paint thinner and 1,1,1 trichloroethane (TCA) are both DNAPLs. As given by Table 2, the disposal rates and exact type of most wastes are not available but estimates for some are given. Based on the information available TCA was chosen as a DNAPL to model. Because of the uncertainty in the total volume of NAPLs disposed of at the landfill, two disposal rates of DNAPLs and two for LNAPLs will be modeled. Disposal rates of 620 gallons per year (gpy), as indicated by Table 2 for TCA, and also 10,000 gpy will be modeled as an indication of possible total DNAPLs disposed of. Migration of benzene and naphthene from a light petroleum product used as a "theoretical" LNAPL at disposal rates of 10,000 and 50,000 gpy.

5.1 Multi-Phase Flow

Once a NAPL has been introduced to the soil, with enough volume to achieve local saturation, it will begin to move downward. If an adequate volume is released downward movement will be sustained until some barrier is reached. LNAPLs will tend to "pile up" and spread laterally when they reach the capillary zone. A DNAPL will continue to move downward through the saturated zone until it reaches a low permeability layer which it cannot penetrate as a separate phase. As the NAPLs travel downward they leave behind amounts of liquid at residual saturation trapped within the pores and as disconnected fingers and blobs. If enough LNAPL or DNAPL has been released it will form a pool at some level.

Water, in this multi-phase flow system, acts as the wetting fluid due to its greater affinity for the solid particles of the porous media. As the non-wetting fluid (NAPL) enters the pore space, it must displace the water. Capillary forces resulting from the interfacial surface tension between NAPL and water are inversely proportional to the pathway "diameter", making it harder for the NAPL to displace the water from smaller pores. The NAPL will initially displace water from the larger pores and gradually occupy smaller and smaller pores until water reaches its residual level. This process can be reversed with water replacing NAPL, leaving NAPL at its residual saturation level. Because of the heterogeneity of the soil, the flow of the NAPL will be very irregular and result in many discontinuous fingers and "blobs" that become trapped.

The depth which a NAPL will penetrate is dependent on several factors, including; NAPL volume and manner released, distance to water table or other barrier, volumetric residual NAPL content, NAPL properties and porous media properties. Horizontal bedding layers of finer soils will promote lateral spreading as it is difficult for the NAPL to penetrate the smaller pores until sufficient pressure head is built up. Once a continuous quantity of NAPL has collected within pore spaces it can only move if the capillary forces from the interfacial surface tension between water and NAPL are overcome. Gravity forces from the difference in density of the NAPL and pore fluid and viscous forces caused by water flowing past a NAPL are two forces which can cause a NAPL to move.

5.2 NAPL Mobility

Sitar (1987) presents criteria to judge the lengths of NAPL fingers or "ganglia" which will be able to move. Vertical migration of NAPL fingers can be evaluated with the Bond Number. The Bond Number is the dimensionless ratio of the buoyancy force per cross sectional area to the capillary pressure.

$$\text{Bond Number} = ([p_i - p_j] * g * L_v * d_t) / \sigma > 4$$

p_i = density of fluid i,j (NAPL and water or air, air density is usually neglected),

g = gravitational constant,

L_v = length of ganglia,

d_t = pore throat diameter, assumed to equal 0.155 of the mean grain diameter,

σ = capillary pressure.

Ganglia shorter than L_v will be stable and not moved by buoyancy forces. This can cause ganglia to stop moving downward and become trapped if the supply of NAPL is discontinued. Also, a LNAPL resting on the water table may be trapped beneath a rising water table. Displacement of one fluid by another is more difficult in fine grained sediments, due to the larger capillary forces. This leads to stable ganglia lengths which are longer for finer grained media.

Displacement of trapped NAPL caused by the viscous force of flowing groundwater can be assessed by comparing the viscous force as water flows across the NAPL to the capillary pressure. Sitar (1987) accomplishes this with another dimensionless criteria:

$$C_a * (L_h * d_t / k) > 4 \quad \text{where:}$$

C_a = Capillary Number

$$= u_w * v / \sigma,$$

L_h = stable NAPL length in the direction of water flow,

d_t = pore throat diameter,

k = hydraulic conductivity for water,

u_w = viscosity of water,

v = Darcy velocity of the groundwater.

When this dimensionless quantity exceeds 4 the NAPL is likely to be displaced. These two criteria can be used to see what may have happened to NAPLs disposed of at Site 7. The following values are used:

$$i = 0.0018 \text{ (Ebasco, 1991),}$$

$$u_w = 1.5 \text{ dynes/cm}^2,$$

$$\sigma \text{ (TCA \& water)} = 45 \text{ dynes/cm (Hunt, 1988),}$$

$$\sigma \text{ (oil \& water)} = 35 \text{ dynes/cm (Daniel, 1993b),}$$

$$\text{fine sand mean grain diameter} = 0.1 \text{ mm}$$

$$d_t = 0.00155 \text{ cm,}$$

$$\rho \text{ (TCA)} = 1.35 \text{ g/cm}^3,$$

$$\rho \text{ (oil)} = 0.75 \text{ g/cm}^3,$$

$$g = 981 \text{ g/cm-sec}^2.$$

	Oil	TCA
$L_v \text{ (m)}$	0.75*	3.4
$L_h \text{ (m)}$	520	670
* stable length of light oil submerged in water.		

Because the NAPLs were most likely placed on or near the water table due to the operations of the landfill, the assumption is made that they easily reach this point. L_h indicates the stable length of a NAPL pool, in the direction of groundwater flow, before it would begin to move. Pools of DNAPL or LNAPL probably do not exceed these lengths given above due to the nature of the way they were placed in the landfill, i.e. discontinuous over time and distributed over a large area. L_v for TCA of 3.4 meters indicates that there could be many trapped ganglia that never made it to the bottom if their supply did not allow it to reach the confining layer at a depth of approximately 4 to 6 meters below the water table. L_v for the LNAPL indicates that a

finger trapped below a rising water table would have to be longer than 0.75 meters before it would begin to move upward. Because of the fairly constant head boundaries assumed at this site, long term water table fluctuations may not occur, however changes in the water level of Little Creek Reservoir would affect water table elevations. Seasonal fluctuations probably result in the LNAPL "smeared" over a range above and below the normal elevation.

5.3 NAPL Modeling

The NAPLs placed in the landfill at Site 7 probably resulted in numerous pools of LNAPL trapped at the water table and DNAPLs trapped at the confining layer. Although as a separate phase they may not be mobile, because of their low solubility's they can continue to be a source of groundwater pollution over a long period of time. In the following sections two different methods will be used to evaluate the history of these pools. First a computer program (Hydrocarbon Spill Screening Model, HSSM) developed to estimate the effects of LNAPLs on groundwater will be used (Charbeneau, 1993). For DNAPLs, a method presented by Johnson and Pankow (1992) will be used to estimate the concentrations within the groundwater and the length of time required for dissolution of DNAPL pools.

5.3.1 LNAPLs

5.3.1.1 Model Description (HSSM)

To determine the migration of LNAPLs constituents HSSM is used to model the effects and fate of 10,000 gpy and 50,000 gpy releases of petroleum hydrocarbons. A brief discussion of HSSM will be presented here, the model is discussed in more detail by Charbeneau (1993). HSSM is based on semi-analytical procedures and uses simplified solution methods for the transport equations. It models the movement of the LNAPL as a separate phase and the migration of a chemical constituent of the oil as well. This chemical constituent of the oil phase can partition between the oil phase, water phase or sorbed phase.

HSSM is actually a combination of three models; KOPT, OILENS and TSGPlume, to provide a single model which can be used to determine the transport of contaminants from a hydrocarbon spill as it travels downward through the vadose zone, collects at the water table and

transfers to the groundwater in which it is transported further. The Kinematic Oily Pollutant Transport (KOPT) model establishes the movement and speed of the oil front and aqueous phase transport as they travel down through the vadose zone. The results of KOPT are the oil content and aqueous phase concentrations as a function of depth and time and the flux of oil and chemical constituent of interest, e.g. benzene or naphthene, to the water table capillary fringe. The OILENS model takes this information and characterizes the formation and spreading of an oil lens as the free phase oil reaches the water table.

OILENS determines the mass flux of the oil and individual constituent into the groundwater resulting from infiltrating water passing through the lens and groundwater/oil contact at the interface between the oil lens and the water table. This then serves as the input to the groundwater contaminant transport portion of HSSM, Transient Source Gaussian Plume (TSGPlume), which models the transport of the dissolved phase contaminants within the aquifer. HSSM can include the effects of degradation by designating a half-life, retardation from partitioning, and the impacts of advection, dispersion and residual saturations on contaminant transport.

5.3.1.2 Model Application

The assumed release pattern is a constant flux of oil into the soil over a given area. Assuming a circular area and an initial ponded depth of six inches (0.15 m) gives a 29 ft (9 m) radius for the 10,000 gallon release and 65 ft (20 m) radius for the 50,000 gallon release. The oil is assumed to infiltrate over a three day period at a constant flux of 2 in/d (0.15 m/d). Table 2 indicates that total hydrocarbon liquid disposal rates were in the range of 50,000 to 60,000 gallons per year. Some of these are DNAPLs and some are LNAPLs.

Modeling releases of 10,000 and 50,000 gallons provides some insight into the migration of these liquids by determining the concentration of an LNAPL constituent in a receptor well. The well is set at 230 meters (750 ft) from the release. This assumes the release occurs at the upper 2/3rds point within the landfill. Assuming disposal rates are constant over a period of years, this would result in numerous pools of LNAPLs scattered over the site. The receptor well

in this modeling effort is set directly downstream from the release. This is surely not the case at Site 7, however, given the number and spatial scattering of the probable LNAPL "releases" lateral dispersion from the separate releases should result in a widespread concentration front. The attempt here is to determine whether or not contaminants from these releases should be detectable by the monitoring wells at the site boundary.

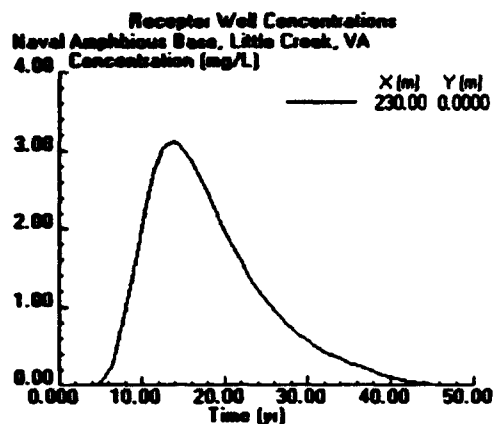
The mobility of some of the less volatile constituents of an LNAPL such as benzene and naphthene from are considered as an example of groundwater contamination from LNAPLs. Benzene was chosen for its higher aqueous solubility (1,780 mg/L) and to represent some of the lighter fractions of the hydrocarbon present in the LNAPL at lower initial concentrations (assumed as 8,000 mg/L of LNAPL). Naphthene was chosen to represent the effects from a combination of the medium fractions of the LNAPL and was assumed to have an aqueous solubility of 300 mg/L with an initial concentration in the LNAPL of 80,000 mg/L.

The LNAPL is assumed to have a viscosity of 4 centipoise (cp), solubility of 35 mg/L, density of 0.75 g/cm^3 and an interfacial tension with water of 35 dynes/cm. An example input file is shown in Appendix D and provides the hydrogeologic and soil parameters. The soil parameters were chosen to be representative of the sandy soil underlying the landfill at Site 7 (Charbeneau, 1993). Because the rate of degradation of the LNAPL or its constituents is difficult to estimate, the model was applied using no degradation and degradation with a half-life of 500 or 1,000 days to show the effects of degradation.

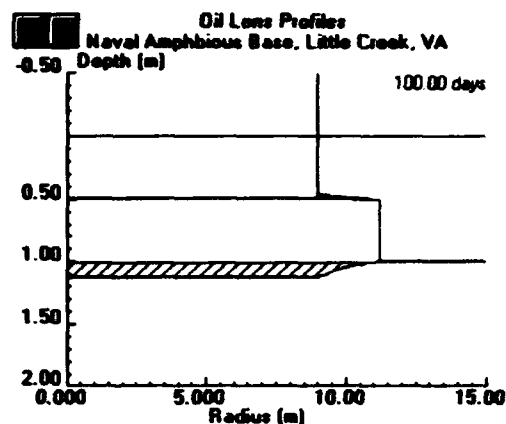
5.3.1.3 Model Results

Figure 18 shows the benzene concentration reaching the well from the 10,000 gallon LNAPL release. The benzene concentration at the receptor well reaches a maximum of 3.2 mg/L at 14 years, shown in Figure 18 (a). Figure 18 (b) and (c) show the development of the LNAPL lens, which remains stationary as trapped free phase LNAPL. Figures 18 (d) and (e) show the transfer of benzene from the lens to the groundwater.

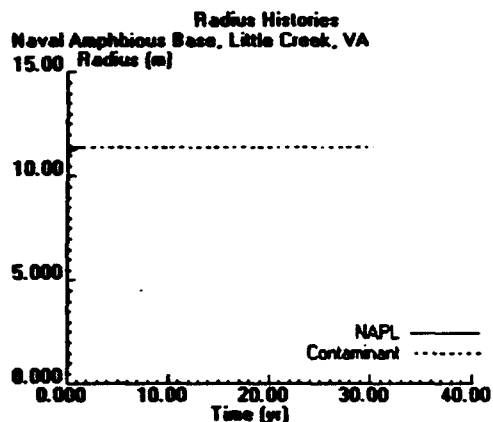
(a)



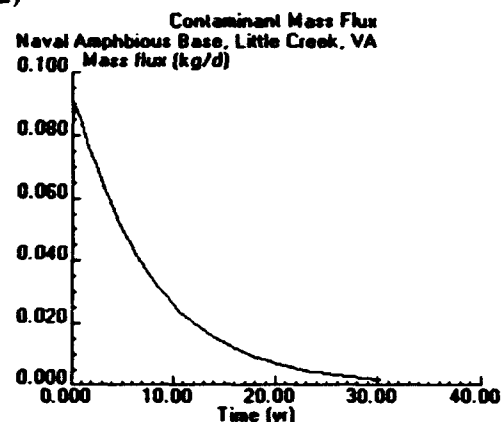
(b)



(c)



(d)



(e)

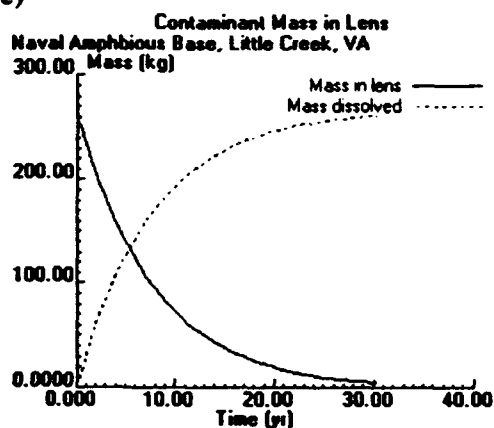


Figure 18. HSSM output for: source radius = 9m, initial constituent conc. in the oil = 8,000 mg/L (benzene), constituent solubility in water = 1,780 mg/L and no degradation.

Including the effects of degradation by designating a half-life ($T_{1/2}$) of 1,000 days reduced the maximum concentration to 0.25 mg/L at 12 years, shown in Figure 19. Using a half-life of 500 days brought C_{\max} down to 0.03 mg/L at 11 years, this graph is not shown. As can be seen by Figure 19, the contaminant mass flux to the aquifer is unaffected by the degradation which is occurring in the aqueous phase.

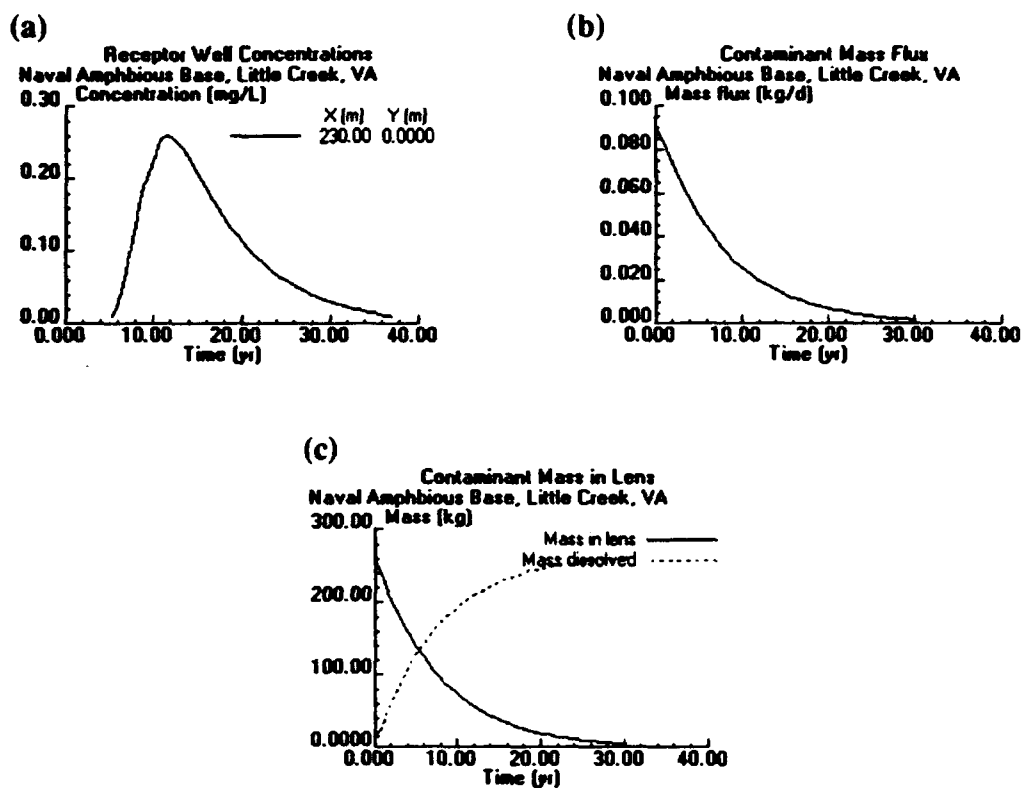


Figure 19. HSSM output for: source radius = 9m, initial constituent conc. in the oil = 8,000 mg/L (benzene), constituent solubility in water = 1,780 mg/L and degradation half life = 1,000d.

Figures 20 and 21 show the monitoring well concentrations and mass flux for naphthene. Figure 21 again includes a degradation half-life of 1,000 days, resulting in approximately an order of magnitude reduction in well concentration from $C_{\max} = 32 \text{ mg/L}$ to 2.7 mg/L . This is similar to the reduction that was seen in the case of benzene with degradation. With a half-life of 500 days $C_{\max} = 0.3 \text{ mg/L}$ at approximately 11 years, this graph is not shown.

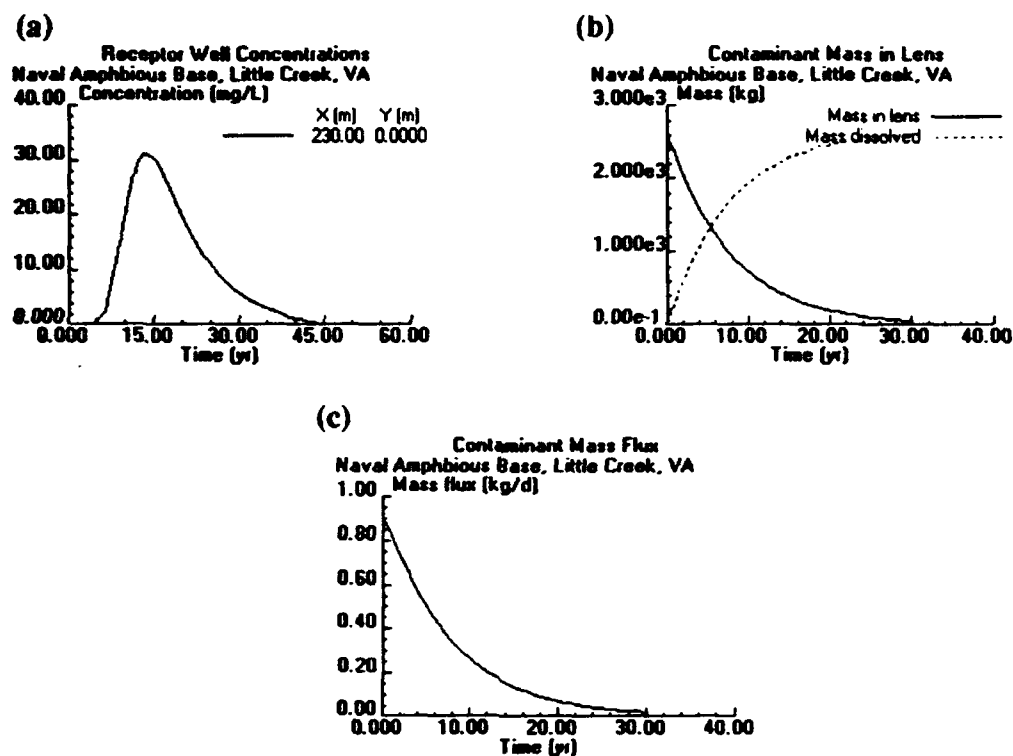


Figure 20. HSSM output for: source radius $\approx 9\text{m}$, initial constituent conc. in the oil = $80,000 \text{ mg/L}$ (naphthene), constituent solubility in water = 300 mg/L and no degradation.

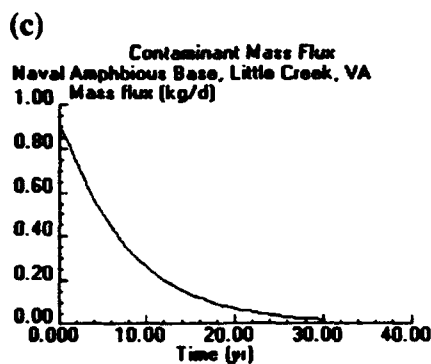
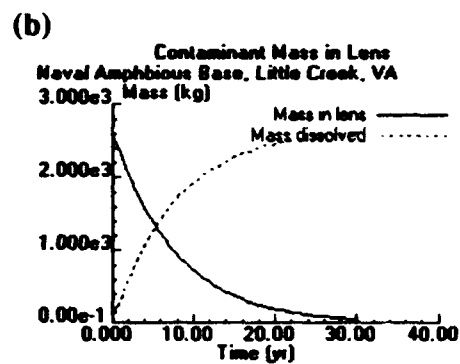
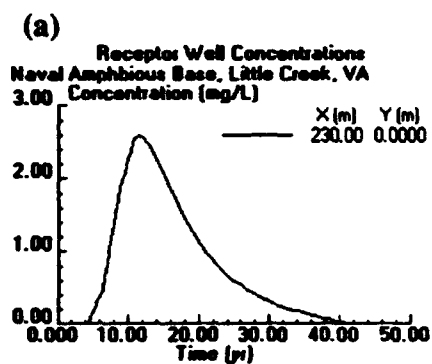


Figure 21. HSSM output for: source radius = 9m, initial constituent conc. in the oil = 80,000 mg/L (naphthene), constituent solubility in water = 300 mg/L and degradation half life= 1,000d.

Figure 22 is the result of the 50,000 gallon release. As can be seen by these figures the mass flux and concentration increases nearly three-fold. Benzene concentrations reached a maximum of 9 mg/L at 15 years. With a $T_{1/2}$ of 1,000 days this maximum was reduced to 0.7 mg/L at 12 years, shown in Figure 23. Again, approximately an order of magnitude reduction in C_{max} , this was further reduced to 0.084 mg/L with a half-life of 500 days.

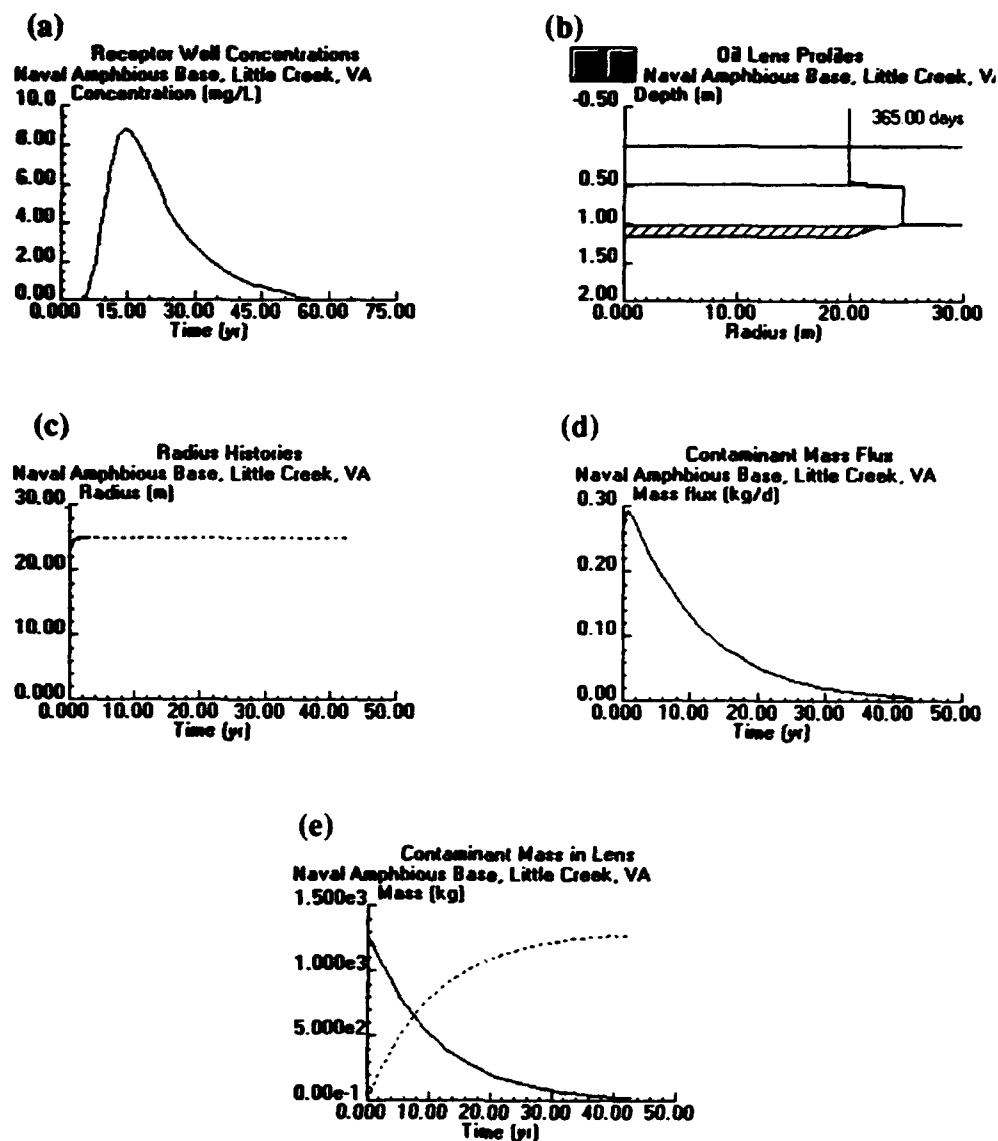


Figure 22. HSSM output for: source radius = 20m, initial constituent conc. in the oil = 8,000 mg/L (benzene), constituent solubility in water = 1,780 mg/L and no degradation.

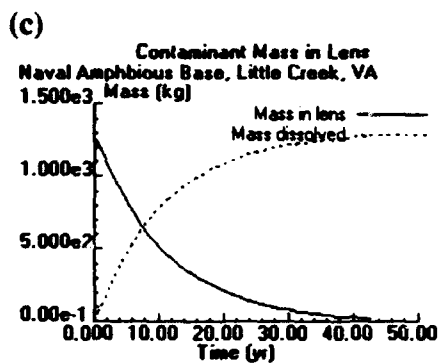
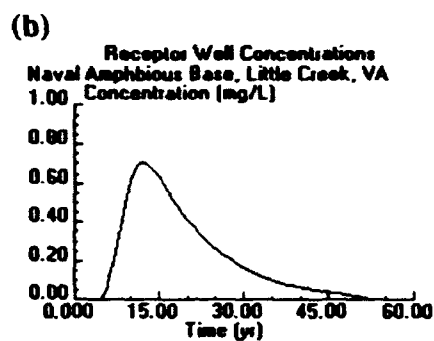
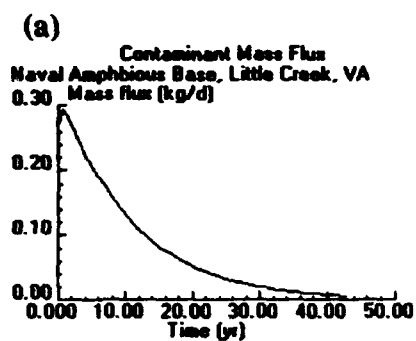


Figure 23. HSSM output for: source radius = 20m, initial constituent conc. in the oil = 8,000 mg/L (benzene), constituent solubility in water = 1,780 mg/L and degradation half life = 1,000d.

Considering the "medium" fraction (naphene), again from the 50,000 gallon release, resulted in a maximum concentration of nearly 90 mg/L at 15 years, Figure 24. Figure 25 includes degradation and shows a C_{\max} of 7 mg/L at 12 years. With a half-life of 500 days, not shown, $C_{\max} = 0.8$ mg/L.

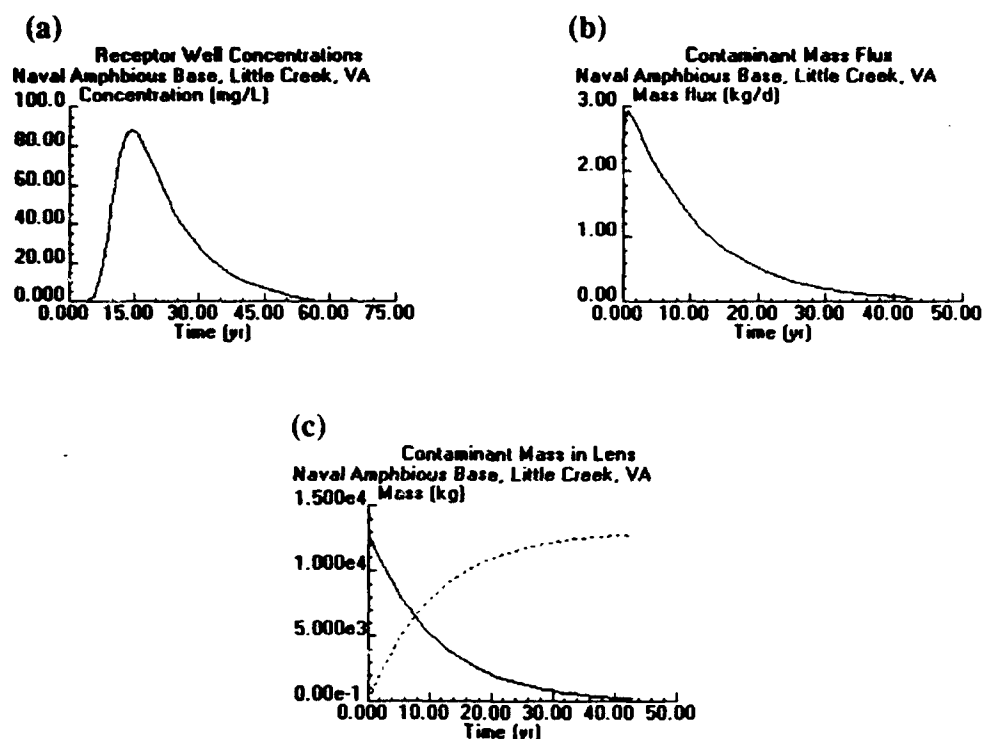


Figure 24. HSSM output for: source radius = 20m, initial constituent conc. in the oil = 80,000 mg/L (naphene), constituent solubility in water = 300 mg/L and no degradation.

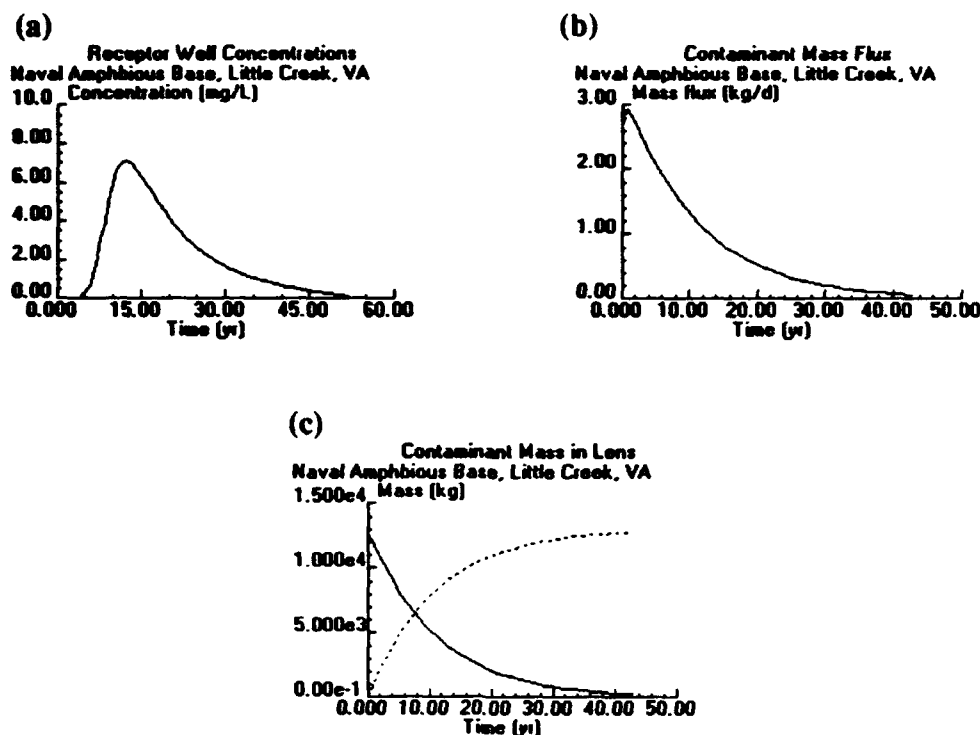


Figure 25. HSSM output for: source radius = 20m, initial constituent conc. in the oil = 80,000 mg/L (naphtene), constituent solubility in water = 300 mg/L and degradation half life = 1,000d.

Several parameters were varied to determine the sensitivity of the maximum well concentrations. Changes to groundwater flow parameters had a large effect on either C_{max} or the time when it occurred (T_{max}). Table 8 below shows some of the variations which occurred. Increasing the flow of water (increasing K or i) or the amount of water present per unit volume (n) has two effects; (1) increased flow accelerates time to C_{max} and (2) decreases the value of C_{max} , perhaps through increased dilution. Decreasing the oil viscosity increases its ability to flow as a free product but does not significantly affect C_{max} . Increasing the residual saturation level allows more oil to be transported, but only affected C_{max} to a small degree. Increasing infiltration actually increased C_{max} , apparently flushing more constituents out of the lens. This sensitivity analysis shows the importance of determining aquifer transport and other parameters.

Table 8. Sensitivity Analysis of Input Parameters

Parameter	Value	%change C_{max}	% change T_{max}
Horizontal Hydraulic Conductivity (m/d)	25	+6	+115
	50	--*	--
	100	-10	-33
Porosity (n)	0.2	+17	nc
	0.3	--	--
	0.4	-11	+14
Hydraulic Gradient	0.0009	+25	+167
	0.0018	--	--
	0.0036	-6	-43
Infiltration Rate (m/d)	0.00035	-17	+7
	0.0007	--	--
	0.0014	+8	-7
Oil/water partition coefficient (K_O)**	150	+28	nc
	300	--	--
	450	-25	nc

* Middle values are those which were used for the analysis.

** $K_O = (MW_i \cdot \text{oil total molar conc.}) / S_i$,

where: MW_i = molecular weight of constituent i,

S_i = solubility of constituent i.

The sum of the benzene and naphthene concentrations represents only a partial contribution of the total petroleum hydrocarbon (TPH) concentration present at the receptor well. The results of this modeling also only account for the more soluble fraction of the total hydrocarbons present within the LNAPL, the heavier fractions are less soluble and more resistant to biodegradation and therefore would tend to contribute to TPH later but for a longer period of time. Unless significant degradation of the LNAPL constituents is occurring then the monitoring wells at Site 7 would be expected to be reporting TPH concentrations at least at the mg/L to tens of mg/L level, or higher. The placement of oils in the landfill was probably reduced in 1969 when waste oil collection

began. This still puts the 1986 and 1990 sampling efforts well within the time of elevated hydrocarbon concentrations in the above figures. These sampling efforts reported TPH concentrations as below minimum detection limits (BMDL) or less than 1 mg/L.

5.3.2 DNAPLs

If enough DNAPL is released and there are no barriers above the water table it will eventually accumulate in pools on top of low permeability layers. Unless enough DNAPL accumulates to overcome the capillary forces at this low permeability layer it will accumulate and spread laterally. As shown above (Sec. 5.2) the pool length would have to exceed 400 meters below Site 7 before it would become mobile due to groundwater flow. DNAPLs can also flow downhill along the low permeability layer if the slope is great enough, the dip of the confining layer should be determined to see if this could be occurring.

5.3.2.1 Model Description

The method presented by Johnson and Pankow (1992) to evaluate the lifetime of the DNAPL pool and groundwater concentrations is based on steady state dissolution of the DNAPL into the groundwater flowing over the pool. The rate of dissolution is dependent upon the length of the pool in the direction of groundwater flow, groundwater velocity, DNAPL solubility, molecular diffusion coefficient and vertical dispersivity. The modeling of contaminant dissolution from DNAPL fingers is considered by Anderson, et al. (1992). Because the fingers have a much larger surface area to mass ratio available to flowing water they have a shorter lifetime. Here only the contribution from the pools will be considered.

Several of the assumptions made by Johnson and Pankow are:

(1) Pool dissolution time is much, much greater than the time it takes groundwater to flow over the pool. This allows use of a steady state form of the advection-dispersion transport equation to be used.

(2) Horizontal transverse mixing processes such as diffusion and dispersion are minimal to the width of the pool, i.e. edge effects can be ignored and a two dimensional form of the advection-dispersion equation can be used:

$$(v)dC/dx = (D_v)d^2C/dz^2$$

where: v = average groundwater velocity,

C = concentration,

x = direction along flow,

z = elevation above pool surface.

D_v = vertical hydrodynamic dispersion coefficient, (m^2/sec)

$$= D_e + va_v$$

D_e = effective aqueous diffusion coefficient, (m^2/sec)

a_v = vertical transverse dispersivity (m)

(3) The DNAPL pool is approximated as a square, with a length to thickness ratio of 100.

(4) The porous media is isotropic.

Assuming the following boundary conditions:

$$C(x, y \gg L_p) = 0, \text{ where } L_p = \text{pool length,}$$

$$C(x = 0, y) = 0,$$

$$C(x, y = 0) = C_{sat}, \text{ where } C_{sat} = \text{solubility limit.}$$

The vertical concentration profile at the downstream edge of the pool ($x = L_p$) is given by:

$$C(L_p, z) = C_{sat} * \text{erfc}[z/(2*(D_v*L_p/v)^{1/2})]$$

The "surface area averaged" mass transfer rate M_a is determined from the following equation:

$$M_a = (v*n)/L_p \int_0^\infty C(L_p, z) dz$$

where n = porosity.

The solution to this is given as:

$$M_a = C_{sat} * n * (4*D_v*v/(\pi*L_p))^{1/2}.$$

The time it takes for the DNAPL pool to completely dissolve, assuming the horizontal dimensions of the pool remain constant is then found by:

$$T_p = (\text{DNAPL mass per unit area})/M_a$$

$$\text{where: DNAPL mass} = V_p * n * p,$$

$$V_p = \text{DNAPL pool volume,}$$

$$p = \text{DNAPL density.}$$

Because M_a is a surface area average mass transfer rate it is affected by the pool length. The mass transfer is driven by the concentration gradient at the interface between the NAPL pool and water. This gradient decreases as the water travels along the pool, i.e., it is greater as the water first begins to pass over the pool than it is after the water has flowed over the pool for some distance. This means that M_a decreases as the pool length increases.

5.3.2.2 Model Application

To determine the vertical hydrodynamic dispersion coefficient (D_v), values for D_e and a_v reported by Johnson and Pankow as applicable for dense chlorinated hydrocarbons were used:

$$D_e = 10^{-10} \text{ m}^2/\text{s},$$

$$a_v = 0.00023 \text{ m.}$$

Using a hydraulic conductivity of 680 ft/day (0.0024 m/s), from the middle of the reported range, and a hydraulic gradient of 0.0018;

$$D_v = D_e + a_v * (ki)$$

$$10^{-10} \text{ m}^2/\text{s} + 0.00023 \text{ m} * (0.0024 \text{ m/s} * 0.0018 \text{ m/m})$$

$$10^{-10} \text{ m}^2/\text{s} + 10^{-9} \text{ m}^2/\text{s}$$

$$1.1 \times 10^{-9} \text{ m}^2/\text{s}.$$

This indicates that the contribution of vertical dispersion ($a_v * v$) is an order of magnitude greater than that of molecular diffusion (D_e).

Following are the dimensions of the two releases to be considered, assuming $n = 0.3$ and pool thickness = $0.01L_p$:

	L_p (m)	Thickness (m)
10,000 gal (40 m ³)	24	0.24
620 gal (2.4 m ³)	6	0.06

Computing M_a using the following values:

$$C_{sat} = 1554 \text{ g/m}^3 \text{ @ } 20^\circ\text{C (Jackson, et al., 1992),}$$

$$n = 0.3,$$

$$D_v = 0.000095 \text{ m}^2/\text{d},$$

$$v = 0.4 \text{ m/d},$$

provides:

	L_p (m)	M_a (g/m ² -d)
10,000 gal	24	0.7
620 gal	6	1.3

5.3.2.3 Model Results

The lifetime of the pools in years can now be computed as:

$$T_p = [(0.01L_p) * n * p] / (365M_a)$$

The density of TCA is $1.35 \times 10^6 \text{ g/m}^3$ (Jackson, et al., 1992).

Using this method the 10,000 and 620 gallon releases would have estimated lifetimes of 380 and 51 years respectively.

The vertical concentration profile at the downgradient edge of the pool can be determined using the equation for $C(L_p, z)$ given in the previous section. Table 9 provides these

concentrations and they are graphed in Figures 26 and 27 to show the concentration profiles for both release configurations. The average concentration for the first 30 cm would be 215 mg/L for both cases. Table 9 shows the concentration profiles for groundwater velocities of 0.1 m/d, 0.4 m/d (shown in graphs) and 1.3 m/d. As can be seen the slower ground water pickups higher concentrations as would be expected from a longer residence time over the DNAPL pool. In fact groundwater velocity controlled the concentration more than the length of the pool for these cases.

The concentrations of TCA seen in a monitoring well would be measured as the vertically mixed average value over the screened interval. If the screened portion of the well did not extend to the base of the aquifer the chance of detecting the DNAPL would not be as good. The location and volume of DNAPL releases is uncertain, however, if the rate of disposal is near that estimated then pools of DNAPL would be scattered about underneath Site 7. This would increase the width and strength of the concentration front at the boundary of Site 7 and provide easier detection. DNAPL reaching the monitoring wells would contribute to the total petroleum hydrocarbon (TPH) concentration and should result in significant levels being detected. However, as discussed earlier, TPH concentrations for the monitoring wells in 1986 and 1990 did not exceed 1 mg/L.

z (meters)	$C(0,z)$ (mg/L)	v (m/day)	Dv (m ² /day)	Lp (meters)	Qcd (mg/L)
0.05	542.302	0.4	9.5E-05	6	1554
0.1	94.8635				
0.15	7.70455				
0.2	0.27884				
0.25	0.00439				
0.3	3E-05				
0.35	8.6E-08				
0.4	1E-10				
z (meters)	$C(0,z)$ (mg/L)	v (m/day)	Dv (m ² /day)	Lp (meters)	Qcd (mg/L)
0.1	542.302	0.1	9.5E-05	6	1554
0.2	94.8635				
0.3	7.70455				
0.4	0.27884				
0.5	0.00439				
0.6	3E-05				
0.7	8.6E-08				
0.8	1E-10				
0.9	0				
z (meters)	$C(0,z)$ (mg/L)	v (m/day)	Dv (m ² /day)	Lp (meters)	Qcd (mg/L)
0.05	141.918	1.3	9.5E-05	6	1554
0.1	1.13917				
0.15	0.00063				
0.2	2.2E-08				
0.25	0				
0.3	0				
0.35	0				
0.4	0				
0.45	0				

Table 9 (a). Vertical concentration profile at downgradient edge of pool. Pool length equals 6 m and groundwater velocities of 0.4, 0.1 and 1.3 m/d are used.

z (meters)	C(z) (mol/L)	v (m/day)	Dv (m ² /day)	Lp (meters)	Csd (mol/L)
0.1	542.302	0.4	9.5E-05	24	1554
0.2	94.8635				
0.3	7.70455				
0.4	0.27884				
0.5	0.00439				
0.6	3E-05				
0.7	8.6E-08				
0.8	1E-10				
0.9	0				
1	0				
z (meters)	C(z) (mol/L)	v (m/day)	Dv (m ² /day)	Lp (meters)	Csd (mol/L)
0.1	993.9	0.1	9.5E-05	24	1554
0.2	542.302				
0.3	248.729				
0.4	94.8635				
0.5	29.8496				
0.6	7.70455				
0.7	1.62435				
0.8	0.27884				
0.9	0.03888				
1	0.00439				
1.2	3E-05				
1.4	8.6E-08				
1.6	1E-10				
1.8	0				
2	0				
z (meters)	C(z) (mol/L)	v (m/day)	Dv (m ² /day)	Lp (meters)	Csd (mol/L)
0.1	141.918	1.3	9.5E-05	24	1554
0.2	1.13917				
0.3	0.00063				
0.4	2.2E-08				
0.5	0				
0.6	0				
0.7	0				
0.8	0				
0.9	0				
1	0				

Table 9 (b). Vertical concentration profile at downgradient edge of pool. Pool length equals 24 m and groundwater velocities of 0.4, 0.1 and 1.3 m/d are used.

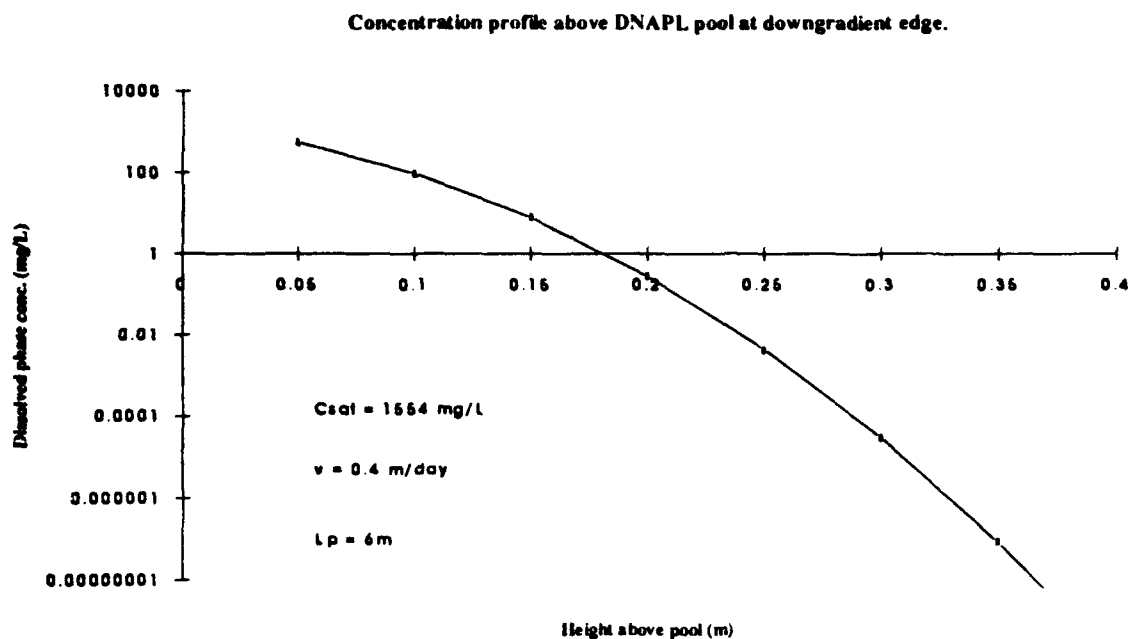


Figure 26. DNAPL concentration profile in groundwater above downgradient edge of 6m pool.

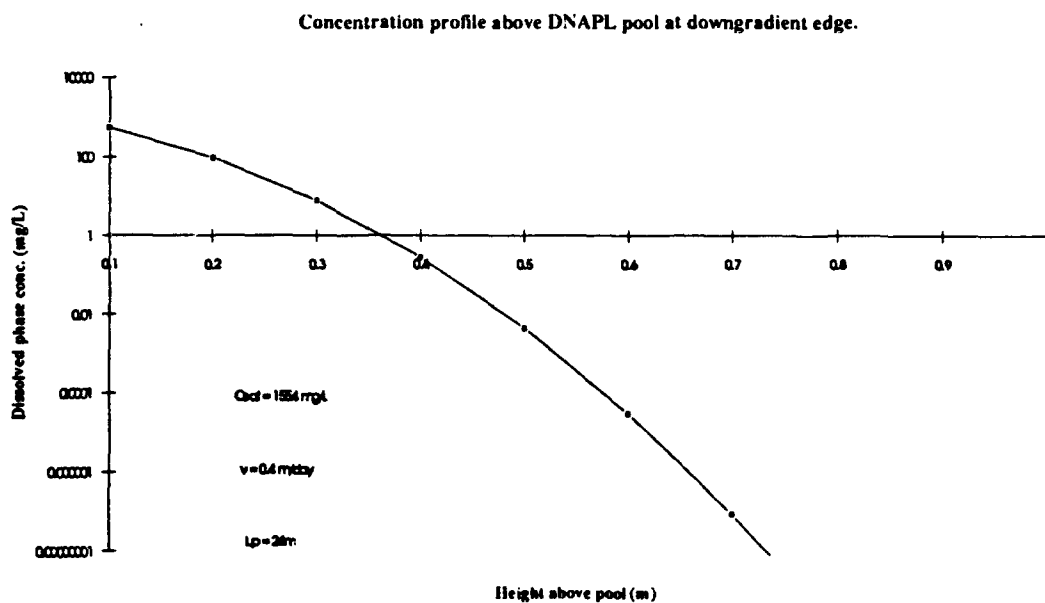


Figure 27. DNAPL concentration profile in groundwater above downgradient edge of 24m pool.

6.0 CONTAMINANT TRANSPORT MODELING

Groundwater flow patterns in the water table aquifer at Site 7 are determined by the two constant head boundaries provided by Little Creek Reservoir and Little Creek Cove. The elevation difference between these two boundaries provides the driving force for groundwater flow at this site. The underlying confining layer further defines the flow pattern by providing a shallow base. Using this conceptual hydrogeologic framework, contaminant transport modeling can provide several benefits but does not supply precise answers. This assumes that the confining layer is effective in preventing contaminant flow. The confining layer could still be subject to diffusion dominated transport. The assumption is also made that the water table aquifer is uniform and homogeneous, even though the boring logs show that this is not the case, especially near the cove.

Models can be used with as much information as is available as long as the results are interpreted keeping in mind the level of information used as input. Model results using a range of parameters help present information which can be used in the decision making process regarding site investigations and remediation efforts.

Contaminant transport models can provide an organized representation of the hydrogeologic and contaminant data available on a site (Taylor, 1986). Models can also help determine which parameters are most important to contaminant transport and sensitive to variation and thus those that should be investigated more carefully. Models can be used to estimate the effects of various actions which may be considered at a site for containment or remediation purposes.

6.1 Objectives

The objective to applying a contaminant transport model to the aquifer underlying Site 7 is to provide insight into migration patterns of the landfill leachate. This information can be used to evaluate the effectiveness of the existing monitoring system and the potential fate of contaminants. Chemical Oxygen Demand (COD) is used as an indicator parameter to model the migration of

leachate from the landfill.

6.2 Model Description

UNMOC simulates the fate and transport of soluble contaminants in an unconfined aquifer and can include the effects of sorption and degradation. The program is a modification of the MOC transport code (Method Of Characteristics, referring to the solution method for the transport differential equations) developed by the United States Geological Survey (USGS), (Charbeneau, 1993).

UNMOC uses a grid of the area to be modeled as an input pattern. The edges of the grid are no-flow boundaries. To establish flow in the grid two "adjacent" aquifers are established which have a set head level. A high leakance value from or to these adjacent aquifers allows a uniform flow field to be established. Little Creek Reservoir is modeled as one of these adjacent aquifers with the head level set as 2.4 m, elevation above sea level. Head in the upper adjacent aquifer is established by the elevation of the water in the reservoir. This value can be adjusted during calibration to allow matching of monitoring well water levels. Head in the lower adjacent aquifer is set to match the mean water level in Little Creek Cove. Warwick and Stoffregen (1991) demonstrated that the grid should be orthogonal to the flow patterns to minimize mass balance errors, this is done in this case.

These constant head boundaries can be established by assigning identification codes to the appropriate cells within the grid. These cells can then be assigned values for leakance, head as in an adjacent aquifer and concentration of substances within the incoming water. The identification codes can also be used to designate recharge from precipitation.

Contaminant mass sources can be modeled in three ways; as wells, as diffuse sources or as mass sources. Wells are centered within a cell with radial flow into or out of the well, this allows modeling of injection or production wells. Diffuse sources are uniformly distributed over a cell and assigned a concentration and infiltration rate. Diffuse sources can be used to model flow from or to ponds or lagoons. Mass sources provide a mass release at a specified rate with no associated inflow of water. An alternative method of introducing a contaminant source is by

designating a source concentration to the recharge associated with the identification codes. This alternative is a modification to the standard UNMOC program (Charbeneau, 1993).

Normally the various transport and flow parameters are "calibrated" using the UNMOC model. Beginning with known or estimated values, initial values are chosen, the model is run and the output is compared with the observed data from monitoring wells. Parameters which affect head levels are first calibrated to establish a uniform flow field. Once this is done the contaminant can be introduced into the model and parameters affecting contaminant transport are calibrated to match an existing plume. In this case there is no plume data to calibrate. Given the short travel distance before contaminants reach the cove and the relatively high groundwater velocities, it is assumed that lateral and longitudinal dispersion have less of an impact than advective flow transport.

UNMOC will allow different values of hydraulic conductivity, aquifer bottom elevation and initial concentration values to be assigned to each cell. In this simulation these values are considered to be homogeneous and constant for the area modeled and initial concentrations are taken as zero. The reservoir and cove are modeled as constant head boundaries. This assumption works well since there should be little long term fluctuation in these levels.

Retardation is allowed by designating a linear sorption coefficient. The retardation factor (R_f) is determined by:

$$R_f = 1 + (p_b/n)K_d$$

where: p_b = bulk density of aquifer,

n = porosity,

K_d = linear sorption coefficient. The effects of contaminant degradation can be included by including a decay time half-life.

Several time periods can be modeled by setting the number of "pumping" periods. This allows a contaminant to be introduced and its source strength can be changed or eliminated in subsequent pumping periods. At the end of each pumping period UNMOC provides the concentration and head levels for each cell. These concentration and head distributions can then

be excerpted into a computer program capable of producing a graphical presentation of the results.

6.3 Model Application

Figure 28 shows the grid set up to model groundwater flow in the water table aquifer at Site 7, cell dimensions are 22 m (E-W) by 26 m (N-S). The grid is 20 cells wide and 28 cells long, aligned orthogonal to the flow pattern shown by Ebasco (1991). The outer rows of cells are no flow boundaries. Little Creek Reservoir and Cove are approximated as constant head boundaries by assigning a row of identification codes as discussed earlier. Recharge from infiltrating precipitation is modeled by assigning another identification code to the remaining cells of the grid. These recharge identification codes also serve as the mechanism to introduce landfill leachate. An example input file is shown in Appendix E.

Values of hydraulic conductivity (33.5 to 335 m/d), porosity (0.3) and aquifer thickness were taken from evaluation of observation well data and reported values (Ebasco, 1991; Applied Environmental, 1993). The base of the aquifer is taken as an elevation of -6 meters. Typical values for bulk density and specific yield were chosen (1.6 g/cm³ and 0.15), (Freeze and Cherry, 1979). Longitudinal and transverse dispersivities were chosen to represent those found for similar aquifers (10m and 3.3m), (Charbeneau, 1993). Because of the relatively short travel distance before groundwater discharges into Little Creek Cove, dispersion effects should have less of an impact on the contaminant transport process compared to advective flow.

Based on the suspected location of the landfill (NEESA, 1984), the area is divided into six longitudinal sections, each section is three cells wide. Each section is assumed to have had waste placed into it for one sixth of the 17 year life of the landfill (1034 days). A total of ten pumping periods are used to model the landfill from 1962 to the present. An initial pumping period, prior to 1962, is used to establish uniform flow between the two constant head boundaries. Then six (1034 day) periods simulate the operational life of the landfill from 1962 to 1979. This is followed by three time periods to 1986 (2190 days), 1991 (1825 days) and 1993 (1278 days). These dates were chosen to coincide with the sampling efforts conducted in 1986 and 1990.

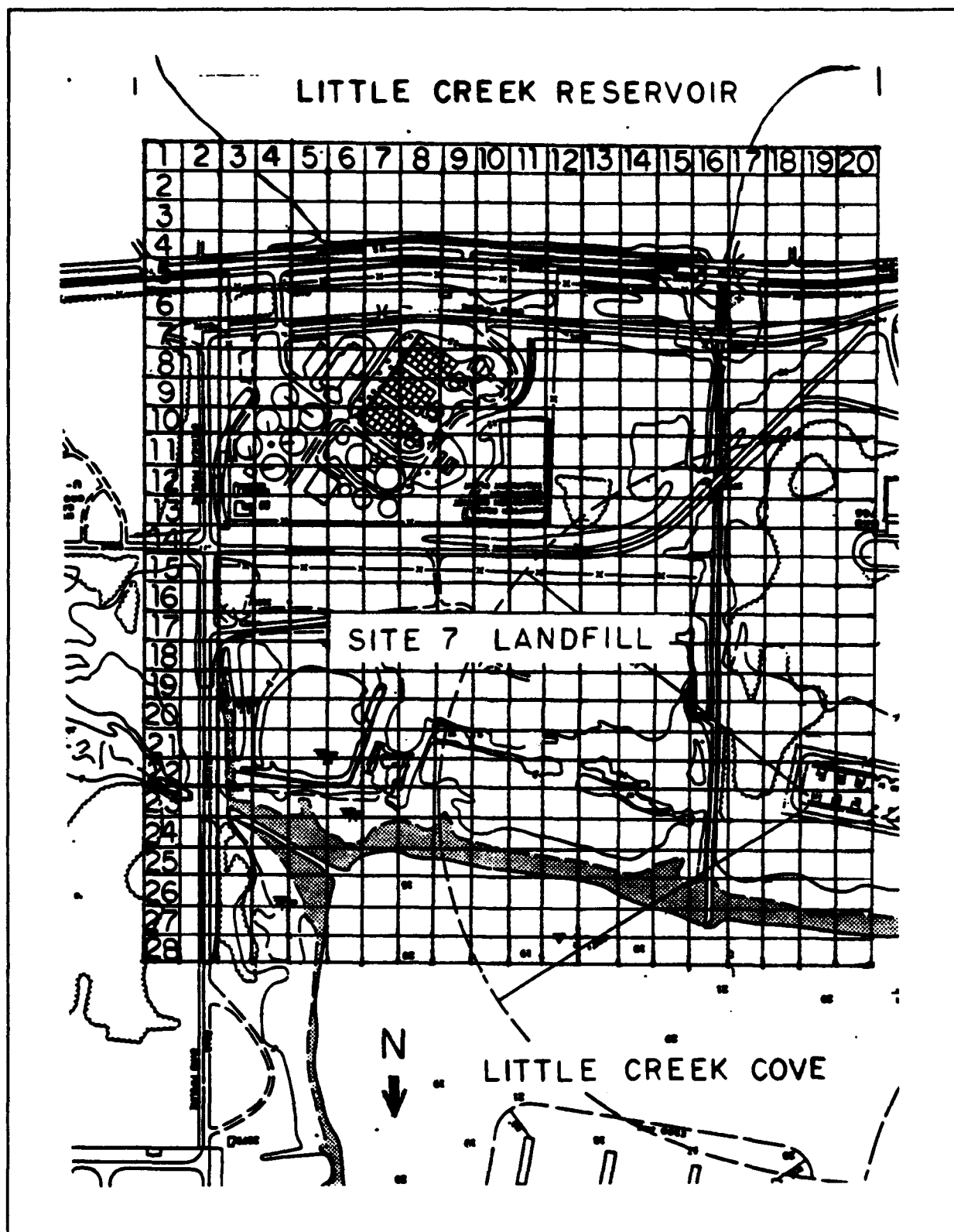


Figure 28. Site 7 modeling grid. Grid cells are 20m by 26m.

Landfill leachate is introduced as a diffuse source by assigning a separate identification code to the six sections of the landfill. This allows the COD concentration from each section to be adjusted separately as they age. Given the ten inches of leachate produced per year from HELP (23.6 L per year per square foot of area) and the estimated leachate COD concentration from Farquhar's method (Table 4) the leachate COD concentration and flow rate from the individual landfill sections area can be determined. This concentration from each section is reduced in each subsequent pumping period as the section ages and produces lower COD concentrations.

Crosser (1987) found R_f from linear isotherms for landfill leachate COD in a silt and clay soil of 9.4 for high COD concentrations and 6.4 for low COD concentrations. Since the water table aquifer underlying Site 7 is sandy it should have a lower R_f . For modeling purposes four cases will be considered; no sorption ($R_f=1$) and $R_f=2, 5$ and 10 . These R_f values correspond to K_d values of 0.19, 0.94 and 1.9, respectively.

Spillman (1989) does not present half-lives for landfill leachate COD, but does present concentration versus distance traveled in the artificial sandy aquifer with a hydraulic gradient of 0.005 m/m. These are provided for a high strength (70,000 mg/L) "fresh" leachate and a lower strength (8,000 mg/L) "aged" leachate. The fresh leachate has two distinct decomposition phases. As shown in Figure 9, in the first 30 m rapid decomposition occurs followed by slower decomposition in the remaining 70 m. The aged leachate having already partially decomposed goes through a slow but gradual decay throughout the entire 100 m.

Assuming a porosity of 0.3 and hydraulic conductivities of 10 m/d and 33.5 m/d and picking points on the graph in Figure 9 where COD has been reduced by 50%, provides a range of values for $T_{1/2}$. The fresh leachate has an estimated range of $T_{1/2}$ of 40 to 120 days for the early phase and 125 to 410 days for the second phase. Estimated $T_{1/2}$ ranges from 180 to 600 days for the aged leachate. Site 7 will be modeled with five values of decay; no decay and $T_{1/2} = 100, 200, 400$ and 1,000 days to determine the effects of a range of half lives.

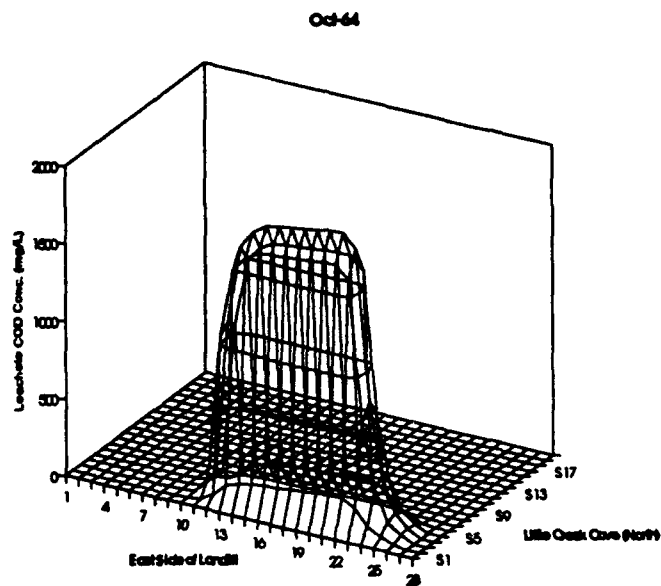
6.4 Model Results and Analysis

Several simulations were made using a range of input values. Retardation factors of 1, 2, 5, and 10 were used with no degradation and degradation half-lives of 100, 200, 400 and 1000 days. Most simulations were made with a hydraulic conductivity of 33.5 meters/day but a few runs were also done with $K = 10$ m/d and 335 m/d. In addition the effect of increased percolation was considered by doubling the rate from 10"/yr to 20"/yr.

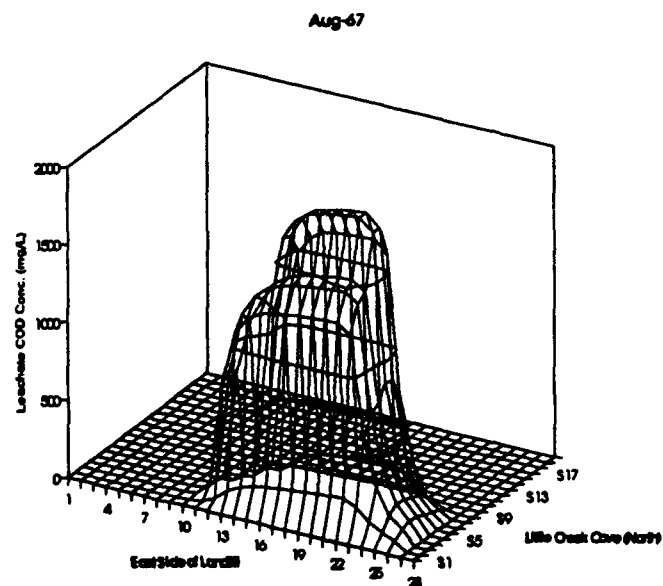
The results of one simulation using $R_f = 5$, $T_{1/2} = 400$ days and $K = 33.5$ m/d is provided in Figure 29 (a) - (i). These figures show the development of the leachate production as the landfill grows from east to west. The graphs show COD concentrations in the 1,500 mg/L range for Figure 29 (a). This is the case for the first of six strips used to model the landfill. Figure 29 (b) shows the groundwater COD levels when now two strips are contributing leachate. Each successive graph up to (f) includes the effects of an additional strip of the landfill. Also the COD concentration from the earlier strips begins to decrease in strength as time passes. The effects of this are shown in Figure 29 (f) where the concentrations on the east side are down below 1,300 mg/L.

Figure 29 (g) and (h) show the estimated COD concentrations approximately at the time of the two sampling efforts (1986 and 1990). The concentrations are lower on the eastern side where more degradation and flushing has occurred, but still range from 400 - 500 mg/L in 86 to ~ 200 mg/L in 90. COD concentrations on the west side range from 1,000 - 1,200 mg/L in 86 to 600 - 700 mg/L in 90.

Figures 29 (a) - (b). UNMOC model results for $R_f = 5$, $T_{1/2} = 400$ days and $K = 33.5$ m/d.

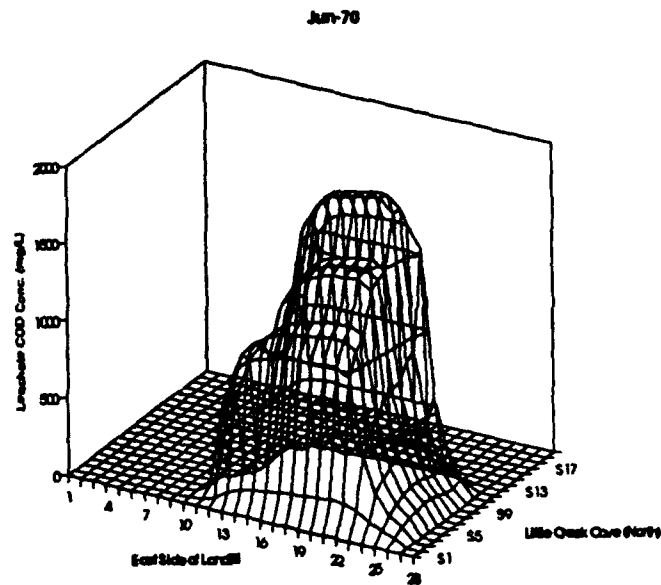


(a)

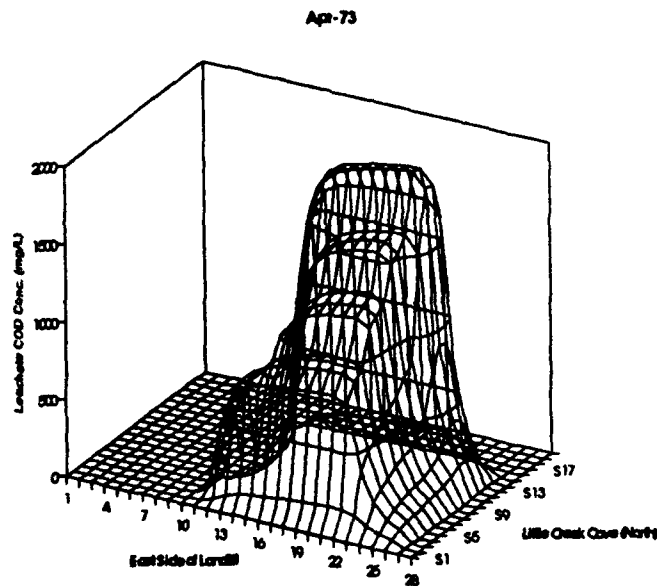


(b)

Figures 29 (c) - (d). UNMOC model results for $R_f = 5$, $T_{1/2} = 400$ days and $K = 33.5$ m/d.

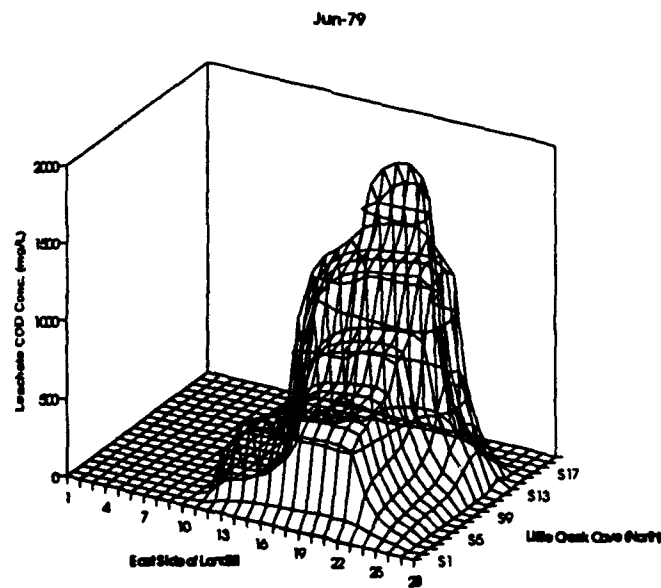
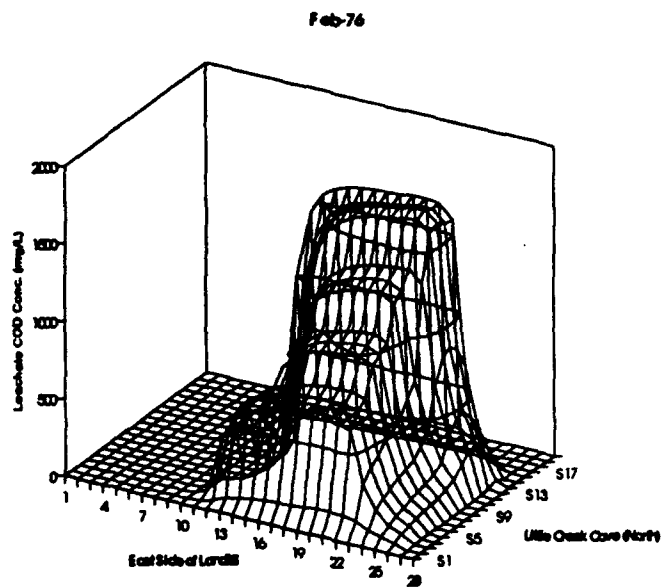


(c)

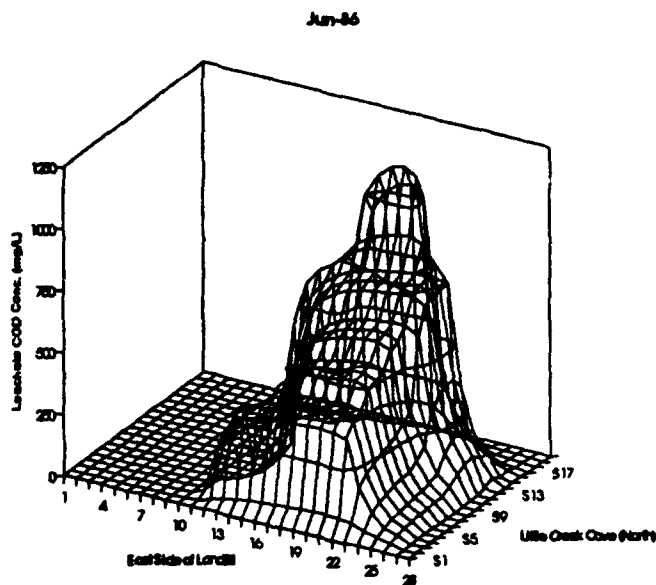


(d)

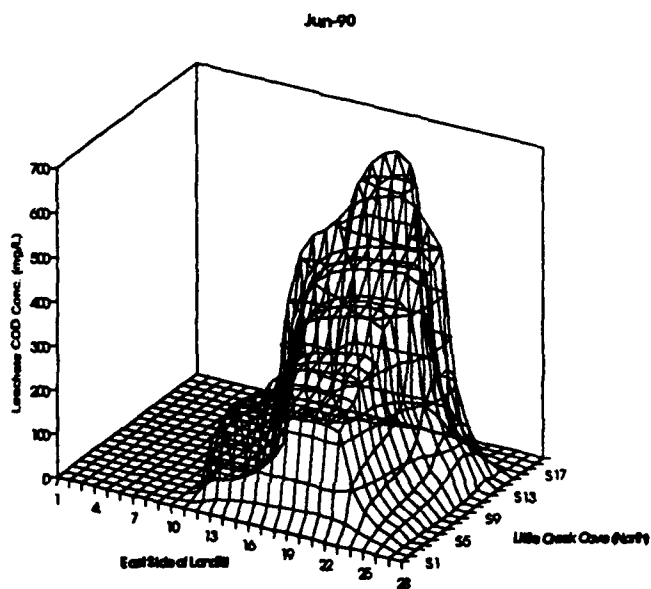
Figures 29 (e) - (f). UNMOC model results for $R_f = 5$, $T_{1/2} = 400$ days and $K = 33.5$ m/d.



Figures 29 (g) - (h). UNMOC model results for $R_f = 5$, $T_{1/2} = 400$ days and $K = 33.5$ m/d.

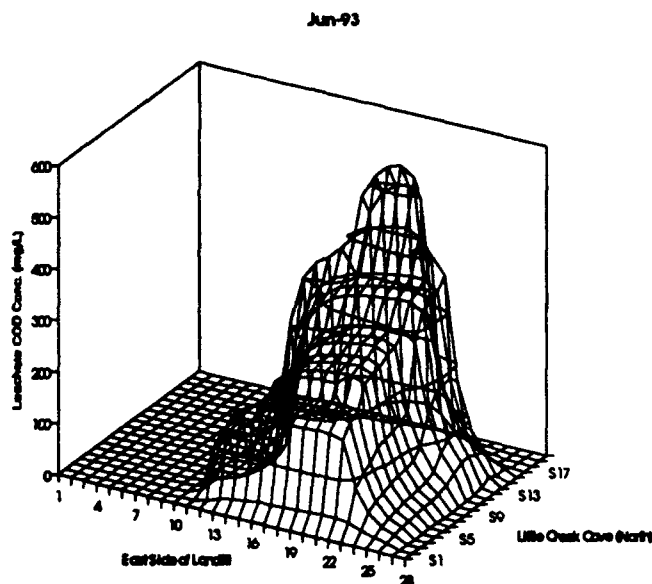


(g)



(h)

Figures 29 (i). UNMOC model results for $R_f = 5$, $T_{1/2} = 400$ days and $K = 33.5$ m/d.



(i)

Figures 30 (a) and (b) present the effects of varying R_f and $T_{1/2}$. Figure 30 (a) indicates that for a given value of R_f the amount of mass which flows into the cove increases as the rate of decay decreases ($T_{1/2}$ increases), i.e., less is degraded and allowed to flow into the cove. For a given value of $T_{1/2}$ more mass of contaminant flows into the cove at lower R_f values, because there is a shorter residence time available for degradation to occur. Figure 30 (b) is really the other side of the coin, as the degradation rate decreases ($T_{1/2}$ increases) so does the % mass decayed. As R_f increases, the contaminant residence time increases and so does the amount degradation. This effect is less pronounced at a half-life of 100 days. The amount of mass stored in the aquifer as sorbed mass or mass in solution is very low, usually less than 4% of mass input. Sorption mass stored was highest (19.4% of mass input) for the case of no decay and high sorption ($R_f = 10$).

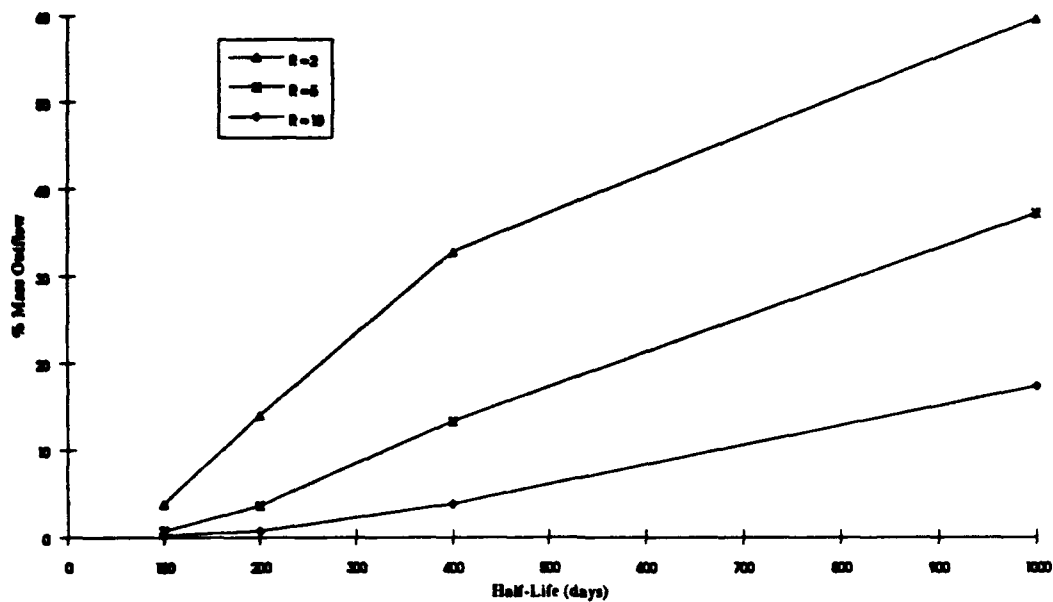


Figure 30 (a). Percent of leachate mass flowing out of the model boundary (into the cove) as a function of degradation rate and retardation.

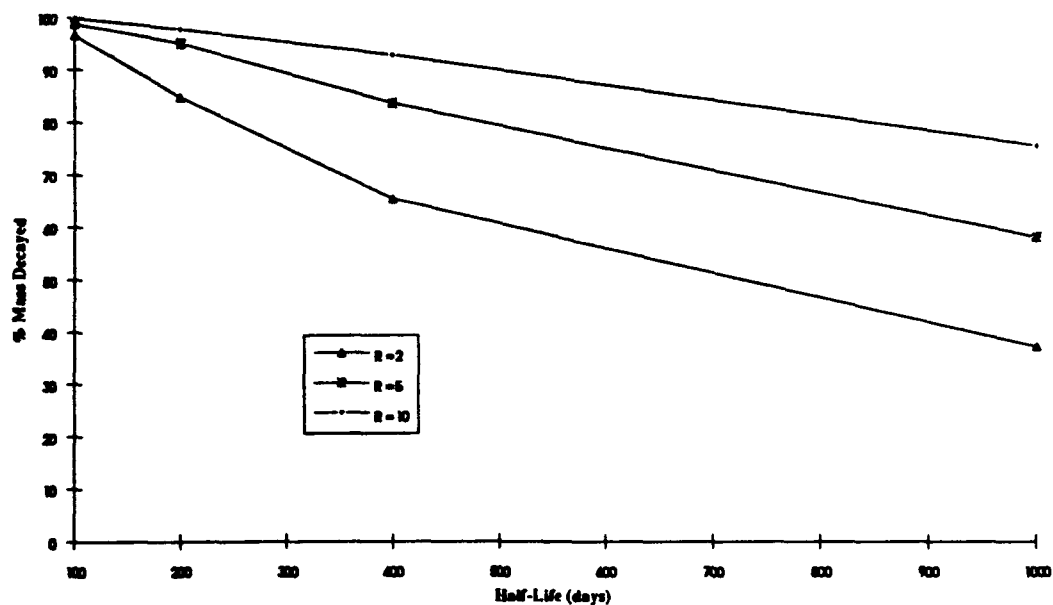


Figure 30 (b). Percent of leachate mass decayed as a function of degradation rate and retardation.

Figure 31 identifies the effect of changing the hydraulic conductivity on the percent of mass which decays and that which flows out. Increasing K reduces the residence time of the leachate and therefore less mass is degraded and more mass flows out into the cove. Because of the limited amount of leachate stored within the aquifer these curves are practically "mirror images" of each other.

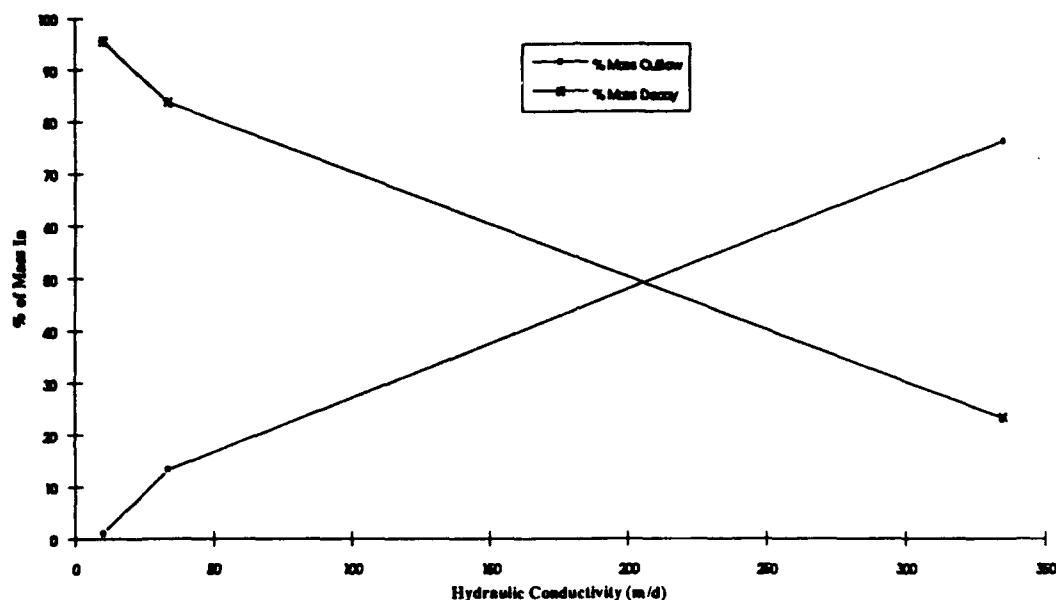


Figure 31. Percent of leachate flowing out and percent of leachate decaying as a function of hydraulic conductivity.

The graphical results of additional computer simulations are included in Appendix F.

6.5 Reversal of Head Gradient

There is some concern that the flow of groundwater beneath Site 7 could be reversed if water levels in Little Creek Reservoir are lowered. Additional modeling was done in an effort to determine the length of time required for sustained low reservoir levels to cause contaminated groundwater to reach the reservoir. This was accomplished with some modifications to the UNMOC code which allowed resetting of the identification codes at each new time period and

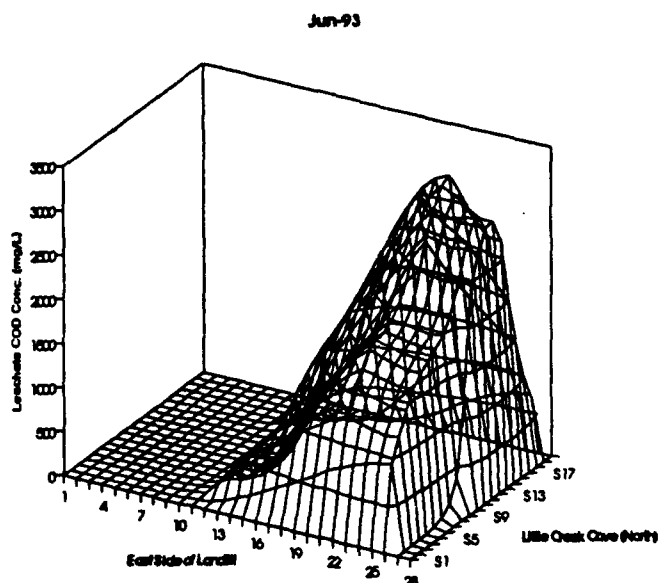
thus the head levels in the adjacent model aquifers can be reset (Charbeneau, 1993). The model was run as before to simulate the landfill from 1962 until 1993, followed by a year where the head difference in the reservoirs was reduced by half. The one year period of reduced head was to simulate the beginning of a drought period and was needed to prevent large gradients from occurring with an immediate reversal which greatly increased computation time. Subsequent one year periods were simulated with the reservoir level 1.5 meters (~ 5 ft) below the water level in the cove, causing a reversal of flow.

Two values were used for the retardation factor ($R_f = 1, 2$), two values for degradation (no degradation and $T_{1/2} = 400$ days) and two values for hydraulic conductivity. The results of the case of ($R_f = 1$, no degradation and $K = 33.5$ m/d) are shown in Figure 32 (a) to (e). Figure 32 (a) is the result of the landfill leachate flowing toward the cove since 1962. Figure 32 (b) is after one year with a 50% reduction in head elevation difference between the reservoir and the cove, but flow is still toward the cove. The subsequent figures (c) to (e) present the COD concentrations for additional one year periods after the head in the reservoir has been dropped below that in the cove.

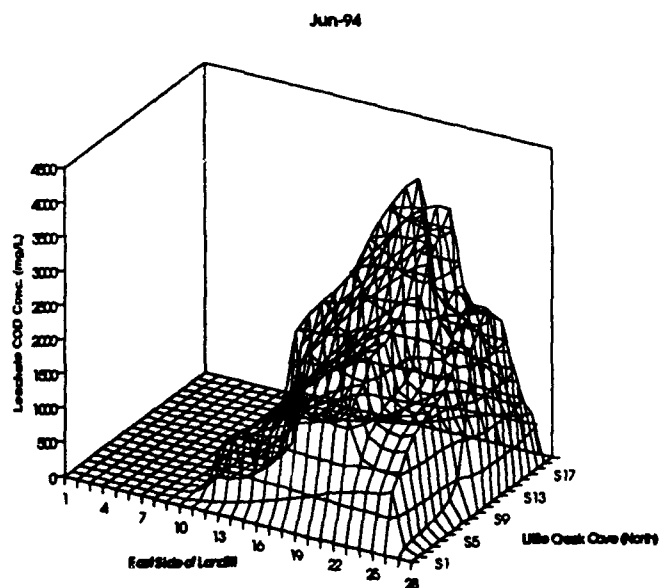
As can be seen by Figure 32(d), by the end of the second year of reversed flow, significant COD concentrations are reaching the reservoir. The time for this to occur was much longer when effects of sorption and decay were added. It took 3 to 4 years for significant COD levels to reach the reservoir when $R_f = 2$ and $T_{1/2} = 400$ days (see Appendix F), and even longer if $R_f = 5$.

The choice of setting reservoir elevation 1.5 meters below the water elevation in the cove was entirely arbitrary as no exact elevation data was available within the time constraints of this report. However, these results show that if it is possible for the reservoir levels to go below that at the cove for a period of time greater than one to two years then migration of landfill leachate contaminants to the reservoir is possible. Increased knowledge of the hydrogeologic setting at Site 7 would make more reliable and meaningful modeling possible with corresponding increased accuracy in the results. The graphical results of additional computer simulations including the effects of flow reversal are included in Appendix F.

Figures 32 (a) - (b). UNMOC model results for $R_f = 1$, no degradation and $K = 33.5$ m/d.

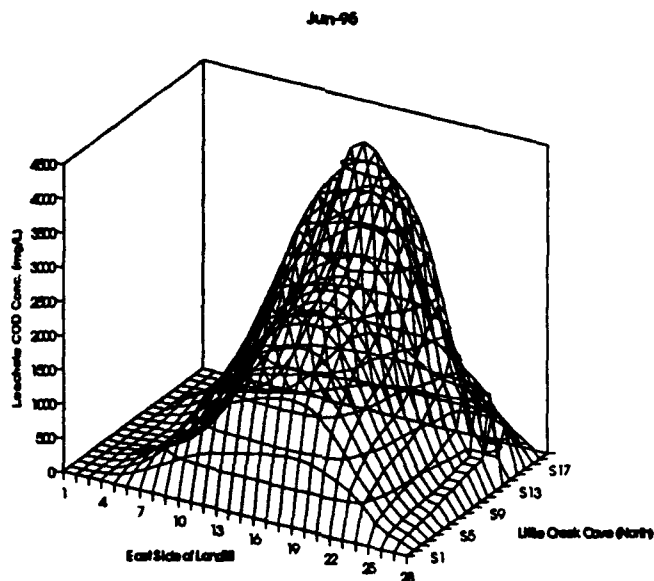


(a) Modeling results from 1962 until 1963 with flow toward cove as before.

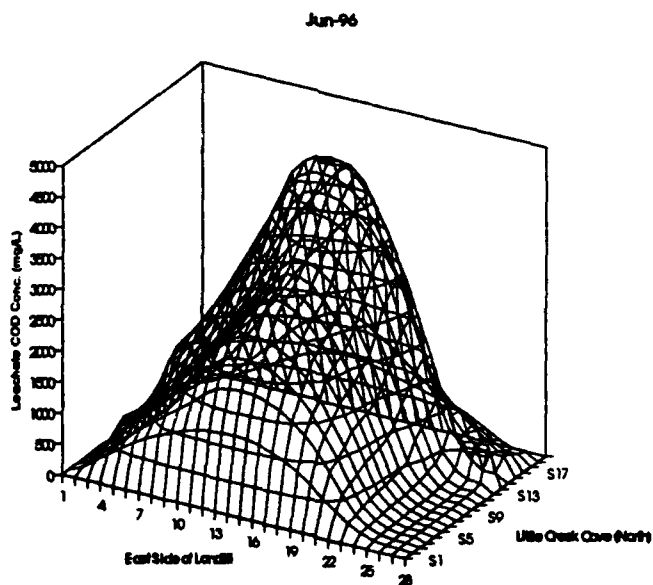


(b) COD concentrations after one year of reduced head, flow remains toward the cove.

Figures 32 (c) - (d). UNMOC model results for $R_f = 1$, no degradation and $K = 33.5$ m/d.

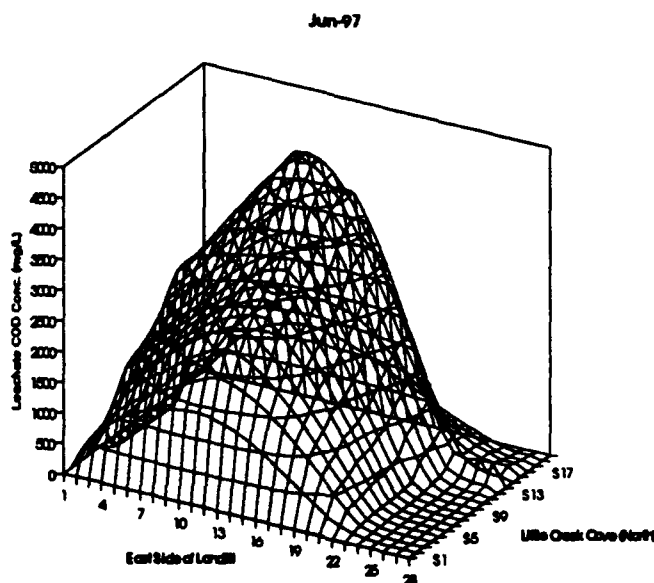


(c) COD concentrations after one year of reversed flow.



(d) COD concentrations after two years of reversed flow.

Figures 32 (e). UNMOC model results for $R_f = 1$, no degradation and $K = 33.5$ m/d.



(e) COD concentrations after three years of reversed flow.

7.0 RECOMMENDATIONS

All model simulations indicate that groundwater contaminated by leachate and NAPLs from the landfill at Site 7 is flowing off-site. Because of the proximity of the cove to the landfill no large groundwater contamination plume develops as a result of this. Surface water quality in the cove is reported as good, (Ebasco, 1990). This raises the question of the rate and amount of dilution in the cove and removal from inflow and outflow within the harbor and tidal circulation, this is an interesting question which is only raised here. Using the case shown in Figure 29 (i), the groundwater currently flowing into the cove would have COD concentrations (200 to 500 mg/L) which have been reduced significantly from previous years (approximately in the range of 1,500 to 2,000 mg/L), due to aging of the landfill and decay of the leachate. What may be happening is

that the contaminant mass loading to the cove is low enough that tidal circulation keeps water quality in the cove from being noticeably impacted. The time scales of groundwater movement and tidal circulation (as well flushing from incoming fresh water) are orders of magnitude apart as may be the volumes of water concerned.

To understand where the leachate is and is not going, a better characterization of the hydrogeology of the site is needed. Geophysical methods can be used to provide a more complete subsurface view of the site. Geophysical methods provide a greater volume of measurements, can provide continuous measurements and can detect anomalies, such as preferential flow paths, which may control the hydrogeological system (Benson, 1993). Once a site characterization has been completed with geophysical methods a drilling and sampling program can be developed to investigate anomalous areas and areas which appear to represent background conditions. This allows a more accurate site characterization while minimizing the number of borings and samples required to achieve the same level of confidence without geophysics. Geophysical logging of the boreholes of new and existing wells can also extract more information about the site and the condition of existing wells.

The objectives of a combined geophysical and physical investigation should be to:

- (a) identify the areal extent of buried wastes at Site 7;
- (b) provide information on waste thickness, buried metals, leachate production, leachate characteristics, etc.;
- (c) possibly provide location of NAPL pools;
- (d) determine the horizontal and vertical flow at the site, including possible preferential flow paths;
- (e) determine hydraulic conductivity, porosity, percent organic carbon, grain size distribution and estimates of dispersivities for the water table aquifer;
- (f) determine the elevation and slope of the top of confining layer including horizontal and vertical variations;

(g) hydraulic conductivity, porosity, percent organic fraction and thickness of the confining layer;

The soils underlying Site 7 are described as sandy with some silty sand, transitioning to a silty clay near Little Creek Cove (CH2M Hill, 1986). This description is supported by the soil boring logs of the monitoring wells installed in 1986 (CH2M Hill, 1986) which show a soft sticky clay to 10 to 13 feet below the surface for wells 7, 8, and 9. The boring logs for these wells indicate that drilling went no deeper. These same wells are completed to a depth of only 7 to 8 feet below the surface. It is possible that a layer of higher hydraulic conductivity material lies below this level and is channeling flow to areas undetectable by the existing monitoring wells.

Another possibility is the existence of preferential flow paths which are horizontally or vertically isolated from the monitoring wells and therefore contaminants flowing through them are not detected. This could be in the form of buried channels filled with a material of higher hydraulic conductivity, a utility line with a bedding layer of rock or gravel and/or naturally occurring sand lenses. If present these features should show up as anomalies in a geophysical survey.

Because of the surface silts and clays, especially along the cove, ground probing radar may not be a suitable geophysical technique for a subsurface survey. However, it may still provide a good survey of the waste and inland areas. Electromagnetic or resistivity methods would probably provide better resolution, especially in the clay soils along the cove. They could be used to perform continuous profiling along a grid to determine areal variations. Sounding can be performed to determine vertical variations to a greater depth. Electromagnetic and resistivity methods measure the electrical conductance and resistivity respectively. Conductance is the reciprocal of resistance, both are functions of the soil type, pore fluid and porosity.

Conductance of the pore fluid can dominate the measurement providing a map of contaminants which have conductance's different than water (Benson, 1993). Salt water intrusion may prevent this methods use along the cove. However, if used it may show areas where intrusion is greater, indicating an area of increased hydraulic connection. Flow of leachate

may also be detected by this method because of the high inorganic concentrations normally associated with landfill leachate.

Pools of hydrocarbons can sometimes be detected by looking for conductivity lows (areas of high resistance) associated with the organic liquids (Benson, 1993). Monitoring wells placed within the landfill at locations indicated by the results of the geophysical survey would allow greater resolution in mapping the groundwater/leachate head and perhaps show where the flow is going. They would also provide convenient leachate sampling locations and observation points for pump tests to determine hydraulic conductivity in the surface aquifer. A phased installation of monitoring wells or piezometers could be incorporated into the investigation to allow information gained from early wells to verify layout assumptions. Later wells could be adjusted if new information was available. Jackson et al., (1993) described a method used to confirm the existence of DNAPL pools, using a the 5 spot well test. Four wells are laid out on the corners of a square and another placed in the center (5 spot layout). A surfactant is pumped into the center well and the four corners pumped to withdraw water which is sampled with a field gas chromatograph to detect the presence of DNAPLs. The surfactant can also be pumped in the four corners and withdrawal pumping in the middle well. This can also serve as a pump test to determine hydraulic conductivity.

Geophysical logging of the boreholes within the confining layer would help determine the continuity of that formation. Rather than relying on laboratory hydraulic conductivity tests of the confining layer soils alone, a pump test should be performed to determine the extent of hydraulic connection between the two aquifers. This would also allow determination of the piezometric head in the underlying aquifer to determine if it discharges to or is recharged by the water table aquifer. A pump test determines the macro hydraulic conductivity as it exists in the formation whereas lab tests may not discover macro properties such as fractures and fissures which could control the hydraulic conductivity. Keller et al., (1985) provide details on a field study which utilized several methods to determine the hydraulic conductivity of a clay layer, including pump tests.

A better characterization of the site hydrogeology and wastes (location, leachate, etc.) is necessary to develop an understanding of past, present and future environmental impacts of the landfill at Site 7. This can be accomplished with a coordinated investigation utilizing geophysical methods, leachate sampling and monitoring wells, aquifer pump tests and physical sampling at well borehole locations. With a thorough understanding of the site hydrogeology, contaminant transport models such as UNMOC can be used to enhance the knowledge of past migration patterns as well as estimate future migration potentials and the effects of possible remediation alternatives.

APPENDIX A

**SITE 7 LANDFILL
MONITORING WELL BORING LOGS**

PROJECT NUMBER W20368		BORING NUMBER LC7-GW1		SHEET OF 	
SOIL BORING LOG					
PROJECT CONFIRMATION STUDY			LOCATION LITTLE CREEK		
ELEVATION 5.70		DRILLING CONTRACTOR ATEC			
DRILLING METHOD AND EQUIPMENT AUGER					
WATER LEVEL AND DATE 5' 4/18/86		START _____		FINISH _____	
LOGGER SEXTON					

ELEVATION	DEPTH BELOW SURFACE (FT)	SAMPLE			STANDARD PENETRATION TEST RESULTS 6"-4"-6" (IN)	SOIL DESCRIPTION NAME, GRADATION OR PLASTICITY, PARTICLE SIZE DISTRIBUTION, COLOR, MOISTURE CONTENT, RELATIVE DENSITY OR CONSISTENCY, SOIL STRUCTURE, MINERALOGY, USCS GROUP SYMBOL	SYMBOLIC LOG	WELL CONSTRUCTION	
		INTERVAL	TYPE AND NUMBER	RECOVERY (FT)					
		0-2	S1	1.8	3-4-4-4	F-M sand w/some clay; ye1. brown (10YR5/4)-ye1. orange(10YR6/6) dry-moist		2 inch PVC	
	5	4-6	S2	2.0	1-0-0-0			GROUT	
								BENTONITE	
	10	9-11	S3	2.0	1-0-0-0	Clay; gr. black(5GY2/1); soft; sticky; wet shell fragments at 9'		SAND	
	15	14-16	S4	2.0	1-0-0-0				
	20								




Figure A1. Site 7 Groundwater Monitoring Well LC7-GW1 Soil Boring Log

PROJECT NUMBER U20368		BORING NUMBER LC7-GW2		SHEET OF	
SOIL BORING LOG					
PROJECT CONFIRMATION STUDY			LOCATION LITTLE CREEK		
ELEVATION 9.97'		DRILLING CONTRACTOR ATEC			
DRILLING METHOD AND EQUIPMENT AUGER					
WATER LEVEL AND DATE 5' 4/17/86		START		FINISH	
LOGGER SEXTON					

ELEVATION	DEPTH BELOW SURFACE (FT)	SAMPLE			STANDARD PENETRATION TEST RESULTS 6"-6"-6" (in)	SOIL DESCRIPTION NAME, GRADATION OR PLASTICITY, PARTICLE SIZE DISTRIBUTION, COLOR, MOISTURE CONTENT, RELATIVE DENSITY OR CONSISTENCY, SOIL STRUCTURE, MINERALOGY, USCS GROUP SYMBOL	SYMBOLIC LOG	WELL CONSTRUCTION
		INTERVAL	TYPE AND NUMBER	RECOVERY (FT)				
		0-2	S1	1.4	2-5-14-14			2 inch PVC
								GROUT
	5	4-6	S2	1.4	7-7-6-9	F-C sand; yell. brown(10YR5/4) -pale yel(10YR6/2); some occasional clay; wet		BENTONITE
	10	9-11	S3	1.4	1-3-3-3			SAND
	15	14-16	S4	2.0	2-4-4-6			
						F-M sand; w/some silt; yel. brown(10YR5/4)		
	20	19-21	S5	1.7	3-3-5-8	As above, but with shell fragments.		
	25							



Figure A2. Site 7 Groundwater Monitoring Well LC7-GW2 Soil Boring Log



PROJECT NUMBER W20368	BORING NUMBER LC7-GW3	SHEET OF
SOIL BORING LOG		

PROJECT CONFIRMATION STUDY LOCATION LITTLE CREEK
ELEVATION 10.27' DRILLING CONTRACTOR ATEC
DRILLING METHOD AND EQUIPMENT AUGER
WATER LEVEL AND DATE 5', 4/17/86 START _____ FINISH _____ LOGGER SEXTON

ELEVATION DEPTH BELOW SURFACE (FT)	SAMPLE			STANDARD PENETRATION TEST RESULTS "6"-6" IN	SOIL DESCRIPTION NAME, GRADATION OR PLASTICITY, PARTICLE SIZE DISTRIBUTION, COLOR, MOISTURE CONTENT, RELATIVE DENSITY OR CONSISTENCY, SOIL STRUCTURE, MINERALOGY, USCS GROUP SYMBOL	SYMBOLIC LOG	WELL CONSTRUCTION	
	INTERVAL	TYPE AND NUMBER	RECOVERY (FT)				2 inch PVC	
5	0-2	S1	1.4	7-5-12-14	F-sand w/some gravel; br. black (5YR2/1); sl. moist		GROUT	
	4-6	S2	2.0	3-3-3-3	Fine sandy clay; olive gr(5Y4/1)- yel brown(10YR4/2); wet at 5'		BENTONITE	
10	9-11	S3	1.8	3-4-5-8	F-M sand w/some c. sand and clay; yel. orange(10YR6/6); wet		SAND	
15	14-16	S4	2.0	3-4-7-9				
20								



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Figure A3. Site 7 Groundwater Monitoring Well LC7-GW3 Soil Boring Log



PROJECT NUMBER W20368	BORING NUMBER LC7-GW4	SHEET OF
SOIL BORING LOG		

PROJECT CONFIRMATION STUDY LOCATION LITTLE CREEK
ELEVATION 6.82' DRILLING CONTRACTOR ATEC
DRILLING METHOD AND EQUIPMENT AUGER
WATER LEVEL AND DATE 2', 4/21/86 START _____ FINISH _____ LOGGER SEXTON

ELEVATION	DEPTH BELOW SURFACE (FT)	SAMPLE			STANDARD PENETRATION TEST RESULTS 6"-6"-6" (IN)	SOIL DESCRIPTION NAME, GRADATION OR PLASTICITY, PARTICLE SIZE DISTRIBUTION, COLOR, MOISTURE CONTENT, RELATIVE DENSITY OR CONSISTENCY, SOIL STRUCTURE, MINERALOGY, USCS GROUP SYMBOL	SYMBOLIC LOG	WELL CONSTRUCTION	
		INTERVAL	TYPE AND NUMBER	RECOVERY (FT)				2 inch PVC	
		0-2	S1	1.4	7-5-4-7	F-M sand w/clay patches; yel. brown (10YR5/4)-olive gray(5Y61); some shell fragments at 5'			GROUT
									BENTONITE
	5	4-6	S2	2.0	2-5-8-10	Fine silty sand; gray(N5)- olive gray(5Y5/2); shell fragments.			SAND
	10	9-11	S3	1.6	2-3-1-1				
	15	14-16	S4	1.7	2-3-1-0				
	20								



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Figure A4. Site 7 Groundwater Monitoring Well LC7-GW4 Soil Boring Log



PROJECT NUMBER W20368	BORING NUMBER LC7-GW5	SHEET OF
SOIL BORING LOG		

PROJECT CONFIRMATION STUDY LOCATION LITTLE CREEK
ELEVATION 6.84' DRILLING CONTRACTOR ATEC
DRILLING METHOD AND EQUIPMENT AUGER
WATER LEVEL AND DATE 4' 4/17/86 START _____ FINISH _____ LOGGER DROWFIELD

ELEVATION	DEPTH BELOW SURFACE (FT)	SAMPLE			STANDARD PENETRATION TEST RESULTS "6"-5" (IN)	SOIL DESCRIPTION NAME, GRADATION OR PLASTICITY, PARTICLE SIZE DISTRIBUTION, COLOR, MOISTURE CONTENT, RELATIVE DENSITY OR CONSISTENCY, SOIL STRUCTURE, MINERALOGY, USCS GROUP SYMBOL	SYMBOLIC LOG	WELL CONSTRUCTION
		INTERVAL	TYPE AND NUMBER	RECOVERY (IN)				
	0-1.5		S1	12	1-1-1	Clayey sand; gray(N5)-yel. brown(10YR5/4); moist, sl. plastic; sl. sticky		2 inch PVC
						Fine silty sand; gray(N4), wet some roots		GROUT
5	3.5-5		S2	8	1-2-3			BENTONITE
						Sandy clay; gray(N3)-gr. gray(5G6/1); soft to sl. plastic; wet		
10	8.5-10		S3	1	1-2-0	Root blocking spoon at 8.5'		SAND
15	13.5-15		S4	14	2-3-5	F-C sand w/some gravel; gray(N5); wet		
20								



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Figure A5. Site 7 Groundwater Monitoring Well LC7-GW5 Soil Boring Log

PROJECT NUMBER W20368		BORING NUMBER LC7-GW6		SHEET 1 OF 1	
SOIL BORING LOG					
PROJECT CONFIRMATION STUDY			LOCATION LITTLE CREEK		
ELEVATION 6.74'			DRILLING CONTRACTOR ATEC		
DRILLING METHOD AND EQUIPMENT AUGER					
WATER LEVEL AND DATE 5' 4/21/86			START		FINISH LOGGER DRONFIELD

ELEVATION	DEPTH BELOW SURFACE (FT)	SAMPLE			STANDARD PENETRATION TEST RESULTS 5'-0"-5' (IN)	SOIL DESCRIPTION NAME, GRADATION OR PLASTICITY, PARTICLE SIZE DISTRIBUTION, COLOR, MOISTURE CONTENT, RELATIVE DENSITY OR CONSISTENCY, SOIL STRUCTURE, MINERALOGY, USCS GROUP SYMBOL	SYMBOLIC LOG	WELL CONSTRUCTION
		INTERVAL	TYPE AND NUMBER	RECOVERY (IN)				
	0-1.5	S1	17	1-2-2	F-M sand w/clay in layers; g-ay(N4) - brown(10YR5/4) moist-wet		2 inch PVC GROUT	
5	3.5-5	S2	12	2-2-1				BENTONITE
10	8.5-10	S3	15	2-2-3	F-M sand w/some f. gravel; gr. gray(5GY6/1)-yel. orange (10YR6/6); wet; some recent shell fragments (not typical Yorktown formation)		SAND	
15	13.5-15	S4	18	3-4-5				
20								



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Figure A6. Site 7 Groundwater Monitoring Well LC7-GW6 Soil Boring Log

PROJECT NUMBER M20368				BORING NUMBER LC7-GW7				SHEET OF			
SOIL BORING LOG											
PROJECT CONFIRMATION STUDY						LOCATION LITTLE CREEK					
ELEVATION 1.96'						DRILLING CONTRACTOR ATEC					
DRILLING METHOD AND EQUIPMENT AUGER											
WATER LEVEL AND DATE 2' 4/22/86						START FINISH LOGGER DROWFIELD					

ELEVATION	DEPTH BELOW SURFACE (FT)	SAMPLE			STANDARD PENETRATION TEST RESULTS 6"-6" (IN)	SOIL DESCRIPTION NAME, GRADATION OR PLASTICITY, PARTICLE SIZE DISTRIBUTION, COLOR, MOISTURE CONTENT, RELATIVE DENSITY OR CONSISTENCY, SOIL STRUCTURE, MINERALOGY, USCS GROUP SYMBOL	SYMBOLIC LOG	WELL CONSTRUCTION
		INTERVAL	TYPE AND NUMBER	RECOVERY (IN)				
		0-1.5	S1	16	1-1-2	F-C sand; gray(N4-N6); roots; wet		2 inch PVC
								GROUT
								BENTONITE
	5	3.5-5	S2	0	1-0-0	Clay w/some silt and sand; gray(N4); very fluid at 3-5'; sticky; sl. plastic elsewhere; wet		SAND
	10	8.5-10	S3	13	1-0-0			
	15	13.5-15	S4	10	1-0-0			
	20							

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Figure A7. Site 7 Groundwater Monitoring Well LC7-GW7 Soil Boring Log



PROJECT NUMBER M20368	BORING NUMBER LC7-GW8	SHEET OF
SOIL BORING LOG		

PROJECT CONFIRMATION STUDY LOCATION LITTLE CREEK
ELEVATION 2.25' DRILLING CONTRACTOR ATEC
DRILLING METHOD AND EQUIPMENT AUGER
WATER LEVEL AND DATE 2' 4/22/86 START _____ FINISH _____ LOGGER DROWFIELD

ELEVATION	DEPTH BELOW SURFACE (FT)	SAMPLE			STANDARD PENETRATION TEST RESULTS 6"-4" (IN)	SOIL DESCRIPTION NAME, GRADATION OR PLASTICITY, PARTICLE SIZE DISTRIBUTION, COLOR, MOISTURE CONTENT, RELATIVE DENSITY OR CONSISTENCY, SOIL STRUCTURE, MINERALOGY, USCS GROUP SYMBOL	SYMBOLIC LOG	WELL CONSTRUCTION
		INTERVAL	TYPE AND NUMBER	RECOVERY (IN)				
		0-1.5	S1	13	2-0-1	F-H sand; gray(N6-N4); roots; wet; clay at bottom		2 inch PVC
								GROUT
								BENTONITE
	5	3.5-5	S2	24	1-0-0	Silty clay w/some sand; v. soft-sl. soft, sl. sticky; gr. gray(5GY4/1)		SAND
	10	8.5-10	S3	24	1-0-0			
	15							



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Figure A8. Site 7 Groundwater Monitoring Well LC7-GW8 Soil Boring Log



PROJECT NUMBER M20358	BORING NUMBER LC7-GW9	SHEET OF
SOIL BORING LOG		

PROJECT CONFIRMATION STUDY LOCATION LITTLE CREEK
ELEVATION 2.83' DRILLING CONTRACTOR ATEC
DRILLING METHOD AND EQUIPMENT AUGER
WATER LEVEL AND DATE 2' 4/23/86 START FINISH LOGGER DROWFIELD

ELEVATION	DEPTH BELOW SURFACE (FT)	SAMPLE			STANDARD PENETRATION TEST RESISTANCE 6"-8"-6" (lb)	SOIL DESCRIPTION NAME, GRADATION OR PLASTICITY, PARTICLE SIZE DISTRIBUTION, COLOR, MOISTURE CONTENT, RELATIVE DENSITY OR CONSISTENCY, SOIL STRUCTURE, MINERALOGY, USCS GROUP SYMBOL	SYMBOLIC LOG	WELL CONSTRUCTION
		INTERVAL	TYPE AND NUMBER	RECOVERY (IN)				
		0-1.5	S1	9	1-1-1	F-M silty sand; gr. gray (5GY4/1); wet		2 Inch PVC
								GROUT
	5	3.5-5	S2	12	3-2-1	Silty clay; gr. gray(5GY4/1); sticky, sl. plastic, sl. soft, clam shell fragments.		BENTONITE
	10	8.5-10	S3	24	1-0-0			SAND
	15							



Figure A9. Site 7 Groundwater Monitoring Well LC7-GW9 Soil Boring Log

APPENDIX B

**HYDROLOGIC EVALUATION OF LANDFILL PERFORMANCE
(HELP) PROGRAM OUTPUT**

HELP MODEL FOR NO COVER (AS IS)

NAB LITTLE CREEK

SITE 7

4 SEP 93

FAIR GRASS

LAYER 1

VERTICAL PERCOLATION LAYER

THICKNESS = 24.00 INCHES
POROSITY = 0.5010 VOL/VOL
FIELD CAPACITY = 0.2837 VOL/VOL
WILTING POINT = 0.1353 VOL/VOL
INITIAL SOIL WATER CONTENT = 0.2837 VOL/VOL
SATURATED HYDRAULIC CONDUCTIVITY = 0.000570000033 CM/SEC

LAYER 2

VERTICAL PERCOLATION LAYER

THICKNESS = 72.00 INCHES
POROSITY = 0.5200 VOL/VOL
FIELD CAPACITY = 0.2942 VOL/VOL
WILTING POINT = 0.1400 VOL/VOL
INITIAL SOIL WATER CONTENT = 0.2942 VOL/VOL
SATURATED HYDRAULIC CONDUCTIVITY = 0.000199999995 CM/SEC

LAYER 3

VERTICAL PERCOLATION LAYER

THICKNESS = 6.00 INCHES
POROSITY = 0.4570 VOL/VOL
FIELD CAPACITY = 0.1309 VOL/VOL
WILTING POINT = 0.0580 VOL/VOL
INITIAL SOIL WATER CONTENT = 0.1309 VOL/VOL
SATURATED HYDRAULIC CONDUCTIVITY = 0.001000000047 CM/SEC

GENERAL SIMULATION DATA

SCS RUNOFF CURVE NUMBER = 60.00
TOTAL AREA OF COVER = 2000000. SQ FT
EVAPORATIVE ZONE DEPTH = 22.00 INCHES
UPPER LIMIT VEG. STORAGE = 11.0220 INCHES
INITIAL VEG. STORAGE = 5.9708 INCHES
INITIAL SNOW WATER CONTENT = 0.0000 INCHES
INITIAL TOTAL WATER STORAGE IN
SOIL AND WASTE LAYERS = 28.7766 INCHES

SOIL WATER CONTENT INITIALIZED BY PROGRAM.

CLIMATOLOGICAL DATA

DEFAULT RAINFALL WITH SYNTHETIC DAILY TEMPERATURES AND
SOLAR RADIATION FOR NORFOLK VIRGINIA

MAXIMUM LEAF AREA INDEX = 2.00
START OF GROWING SEASON (JULIAN DATE) = 101
END OF GROWING SEASON (JULIAN DATE) = 310

NORMAL MEAN MONTHLY TEMPERATURES, DEGREES FAHRENHEIT

JAN/JUL -----	FEB/AUG -----	MAR/SEP -----	APR/OCT -----	MAY/NOV -----	JUN/DEC -----
39.90	41.10	48.50	58.20	66.40	74.30
78.40	77.70	72.20	61.30	51.90	43.50

AVERAGE MONTHLY VALUES IN INCHES FOR YEARS 74 THROUGH 78

	JAN/JUL	FEB/AUG	MAR/SEP	APR/OCT	MAY/NOV	JUN/DEC
	-----	-----	-----	-----	-----	-----
PRECIPITATION						

TOTALS	4.02	2.52	5.02	2.72	3.98	3.64
	6.26	3.58	3.38	2.98	2.99	3.33
STD. DEVIATIONS						
	1.45	1.09	2.13	1.21	0.71	2.94
	4.32	3.01	1.43	1.93	1.79	0.70
RUNOFF						

TOTALS	0.000	0.000	0.000	0.000	0.000	0.000
	0.060	0.004	0.000	0.000	0.019	0.000
STD. DEVIATIONS						
	0.000	0.000	0.000	0.000	0.000	0.000
	0.094	0.009	0.000	0.000	0.042	0.000
EVAPOTRANSPIRATION						

TOTALS	1.528	2.001	2.918	2.932	4.241	4.260
	4.094	3.789	3.690	1.964	1.621	1.427
STD. DEVIATIONS						
	0.080	0.204	0.498	0.844	1.190	1.890
	1.792	1.951	1.511	0.604	0.587	0.183
PERCOLATION FROM LAYER 3						

TOTALS	0.6878	1.0202	1.1649	1.3785	1.0122	0.7016
	0.9488	0.9953	0.6675	0.4770	0.4412	0.4774
STD. DEVIATIONS						
	0.7973	1.0528	0.8082	0.8897	0.5208	0.3153
	0.9457	0.8714	0.5070	0.2946	0.1912	0.3476

AVERAGE ANNUAL TOTALS & (STD. DEVIATIONS) FOR YEARS 74 THRU 78

	(INCHES)	(CU. FT.)	PERCENT
PRECIPITATION	44.44 (7.25)	7406666.	100.00
RUNOFF	0.082 (0.089)	13724.	0.19
EVAPOTRANSPIRATION	34.466 (2.75)	5744266.	77.56
PERCOLATION FROM LAYER 3	9.9725 (5.39)	1662088.	22.44
CHANGE IN WATER STORAGE	-0.080 (3.35)	-13412.	-0.18

PEAK DAILY VALUES FOR YEARS 74 THROUGH 78

	(INCHES)	(CU. FT.)
PRECIPITATION	3.81	635000.0
RUNOFF	0.212	35388.8
PERCOLATION FROM LAYER 3	0.1943	32377.3
SNOW WATER	1.42	236666.7
MAXIMUM VEG. SOIL WATER (VOL/VOL)		0.4409
MINIMUM VEG. SOIL WATER (VOL/VOL)		0.1350

FINAL WATER STORAGE AT END OF YEAR 78

LAYER	(INCHES)	(VOL/VOL)
1	6.51	0.2714
2	21.93	0.3046
3	1.21	0.2020

SNOW WATER 0.00

HELP MODEL FOR COMPACTED CLAY COVER

NAB LITTLE CREEK
SITE 7 W/COVER
4 SEP 93

FAIR GRASS

LAYER 1

VERTICAL PERCOLATION LAYER

THICKNESS = 24.00 INCHES
POROSITY = 0.5010 VOL/VOL
FIELD CAPACITY = 0.2837 VOL/VOL
WILTING POINT = 0.1353 VOL/VOL
INITIAL SOIL WATER CONTENT = 0.2837 VOL/VOL
SATURATED HYDRAULIC CONDUCTIVITY = 0.000570000033 CM/SEC

LAYER 2

LATERAL DRAINAGE LAYER

THICKNESS = 12.00 INCHES
POROSITY = 0.3178 VOL/VOL
FIELD CAPACITY = 0.0391 VOL/VOL
WILTING POINT = 0.0200 VOL/VOL
INITIAL SOIL WATER CONTENT = 0.0391 VOL/VOL
SATURATED HYDRAULIC CONDUCTIVITY = 0.000499999966 CM/SEC
SLOPE = 2.00 PERCENT
DRAINAGE LENGTH = 200.0 FEET

LAYER 3

BARRIER SOIL LINER

THICKNESS = 24.00 INCHES
POROSITY = 0.4300 VOL/VOL
FIELD CAPACITY = 0.3663 VOL/VOL
WILTING POINT = 0.2802 VOL/VOL
INITIAL SOIL WATER CONTENT = 0.4300 VOL/VOL
SATURATED HYDRAULIC CONDUCTIVITY = 0.000000100000 CM/SEC

LAYER 4

VERTICAL PERCOLATION LAYER

THICKNESS = 24.00 INCHES
POROSITY = 0.4096 VOL/VOL
FIELD CAPACITY = 0.2466 VOL/VOL
WILTING POINT = 0.1353 VOL/VOL
INITIAL SOIL WATER CONTENT = 0.2466 VOL/VOL
SATURATED HYDRAULIC CONDUCTIVITY = 0.000009500000 CM/SEC

LAYER 5

VERTICAL PERCOLATION LAYER

THICKNESS = 72.00 INCHES
POROSITY = 0.5200 VOL/VOL
FIELD CAPACITY = 0.2942 VOL/VOL
WILTING POINT = 0.1400 VOL/VOL
INITIAL SOIL WATER CONTENT = 0.2766 VOL/VOL
SATURATED HYDRAULIC CONDUCTIVITY = 0.000199999995 CM/SEC

LAYER 6

VERTICAL PERCOLATION LAYER

THICKNESS = 6.00 INCHES
POROSITY = 0.4570 VOL/VOL
FIELD CAPACITY = 0.1309 VOL/VOL
WILTING POINT = 0.0580 VOL/VOL
INITIAL SOIL WATER CONTENT = 0.1309 VOL/VOL
SATURATED HYDRAULIC CONDUCTIVITY = 0.001000000047 CM/SEC

GENERAL SIMULATION DATA

```

SCS RUNOFF CURVE NUMBER      = 70.00
TOTAL AREA OF COVER          = 2000000. SQ FT
EVAPORATIVE ZONE DEPTH       = 22.00 INCHES
UPPER LIMIT VEG. STORAGE     = 11.0220 INCHES
INITIAL VEG. STORAGE         = 7.6609 INCHES
INITIAL SNOW WATER CONTENT   = 0.0000 INCHES
INITIAL TOTAL WATER STORAGE IN
  SOIL AND WASTE LAYERS      = 44.2142 INCHES
  
```

SOIL WATER CONTENT INITIALIZED BY PROGRAM.

CLIMATOLOGICAL DATA

```

DEFAULT RAINFALL WITH SYNTHETIC DAILY TEMPERATURES AND
SOLAR RADIATION FOR  NORFOLK      VIRGINIA
MAXIMUM LEAF AREA INDEX      = 2.00
START OF GROWING SEASON (JULIAN DATE) = 101
END OF GROWING SEASON (JULIAN DATE)  = 310
  
```


AVERAGE ANNUAL TOTALS & (STD. DEVIATIONS) FOR YEARS 74 THRU 78

	(INCHES)	(CU. FT.)	PERCENT
	-----	-----	-----
PRECIPITATION	44.44 (7.257)	7406666.	100.00
RUNOFF	3.746 (3.938)	624254.	8.43
EVAPOTRANSPIRATION	37.753 (4.971)	6292234.	84.95
LATERAL DRAINAGE FROM LAYER 2	1.0747 (0.3076)	179119.	2.42
PERCOLATION FROM LAYER 3	2.2823 (0.2522)	380389.	5.14
PERCOLATION FROM LAYER 6	1.9652 (0.3812)	327533.	4.42
CHANGE IN WATER STORAGE	-0.099 (4.007)	-16471.	-0.22

PEAK DAILY VALUES FOR YEARS 74 THROUGH 78

	(INCHES)	(CU. FT.)
PRECIPITATION	3.81	635000.0
RUNOFF	2.465	410825.9
LATERAL DRAINAGE FROM LAYER 2	0.0066	1099.9
PERCOLATION FROM LAYER 3	0.0085	1422.3
HEAD ON LAYER 3	36.3	
PERCOLATION FROM LAYER 6	0.0066	1103.9
SNOW WATER	1.42	236666.7
MAXIMUM VEG. SOIL WATER (VOL/VOL)	0.5010	
MINIMUM VEG. SOIL WATER (VOL/VOL)	0.1350	

FINAL WATER STORAGE AT END OF YEAR 78

LAYER	(INCHES)	(VOL/VOL)
1	6.65	0.2769
2	3.81	0.3178
3	10.32	0.4300
4	7.37	0.3071
5	21.16	0.2939
6	1.17	0.1954

SNOW WATER 0.00

HELP MODEL WITH COMPOSITE LINER (FML & CCL)

NAB LITTLE CREEK
SITE 7 W/COVER
4 SEP 93

FAIR GRASS

LAYER 1

VERTICAL PERCOLATION LAYER

THICKNESS = 24.00 INCHES
POROSITY = 0.5010 VOL/VOL
FIELD CAPACITY = 0.2837 VOL/VOL
WILTING POINT = 0.1353 VOL/VOL
INITIAL SOIL WATER CONTENT = 0.2837 VOL/VOL
SATURATED HYDRAULIC CONDUCTIVITY = 0.000570000033 CM/SEC

LAYER 2

LATERAL DRAINAGE LAYER

THICKNESS = 12.00 INCHES
POROSITY = 0.3178 VOL/VOL
FIELD CAPACITY = 0.0391 VOL/VOL
WILTING POINT = 0.0200 VOL/VOL
INITIAL SOIL WATER CONTENT = 0.0391 VOL/VOL
SATURATED HYDRAULIC CONDUCTIVITY = 0.000499999966 CM/SEC
SLOPE = 2.00 PERCENT
DRAINAGE LENGTH = 200.0 FEET

LAYER 3

BARRIER SOIL LINER WITH FLEXIBLE MEMBRANE LINER

THICKNESS = 24.00 INCHES
POROSITY = 0.4300 VOL/VOL
FIELD CAPACITY = 0.3663 VOL/VOL
WILTING POINT = 0.2802 VOL/VOL
INITIAL SOIL WATER CONTENT = 0.4300 VOL/VOL
SATURATED HYDRAULIC CONDUCTIVITY = 0.000000100000 CM/SEC
LINER LEAKAGE FRACTION = 0.00010000

LAYER 4

VERTICAL PERCOLATION LAYER

THICKNESS = 24.00 INCHES
POROSITY = 0.4096 VOL/VOL
FIELD CAPACITY = 0.2466 VOL/VOL
WILTING POINT = 0.1353 VOL/VOL
INITIAL SOIL WATER CONTENT = 0.1641 VOL/VOL
SATURATED HYDRAULIC CONDUCTIVITY = 0.000009500000 CM/SEC

LAYER 5

VERTICAL PERCOLATION LAYER

THICKNESS = 72.00 INCHES
POROSITY = 0.5200 VOL/VOL
FIELD CAPACITY = 0.2942 VOL/VOL
WILTING POINT = 0.1400 VOL/VOL
INITIAL SOIL WATER CONTENT = 0.1451 VOL/VOL
SATURATED HYDRAULIC CONDUCTIVITY = 0.000199999995 CM/SEC

LAYER 6

VERTICAL PERCOLATION LAYER

THICKNESS = 6.00 INCHES
POROSITY = 0.4570 VOL/VOL
FIELD CAPACITY = 0.1309 VOL/VOL
WILTING POINT = 0.0580 VOL/VOL
INITIAL SOIL WATER CONTENT = 0.0842 VOL/VOL
SATURATED HYDRAULIC CONDUCTIVITY = 0.001000000047 CM/SEC

GENERAL SIMULATION DATA

SCS RUNOFF CURVE NUMBER = 70.00
TOTAL AREA OF COVER = 2000000. SQ FT
EVAPORATIVE ZONE DEPTH = 22.00 INCHES
UPPER LIMIT VEG. STORAGE = 11.0220 INCHES
INITIAL VEG. STORAGE = 8.8341 INCHES
INITIAL SNOW WATER CONTENT = 0.0000 INCHES
INITIAL TOTAL WATER STORAGE IN
SOIL AND WASTE LAYERS = 32.4923 INCHES

SOIL WATER CONTENT INITIALIZED BY PROGRAM.

CLIMATOLOGICAL DATA

DEFAULT RAINFALL WITH SYNTHETIC DAILY TEMPERATURES AND
SOLAR RADIATION FOR NORFOLK VIRGINIA

MAXIMUM LEAF AREA INDEX = 2.00
START OF GROWING SEASON (JULIAN DATE) = 101
END OF GROWING SEASON (JULIAN DATE) = 310

AVERAGE ANNUAL TOTALS & (STD. DEVIATIONS) FOR YEARS 74 THRU 78

	(INCHES)	(CU. FT.)	PERCENT
PRECIPITATION	44.44 (7.257)	7406666.	100.00
RUNOFF	5.083 (4.710)	847147.	11.44
EVAPOTRANSPIRATION	38.659 (4.392)	6443120.	86.99
LATERAL DRAINAGE FROM LAYER 2	1.2057 (0.2880)	200949.	2.71
PERCOLATION FROM LAYER 3	0.0002 (0.00)	40.	0.00
PERCOLATION FROM LAYER 6	0.0001 (0.00)	18.	0.00
CHANGE IN WATER STORAGE	-0.507 (3.592)	-84568.	-1.14

PEAK DAILY VALUES FOR YEARS 74 THROUGH 78

	(INCHES)	(CU. FT.)
	-----	-----
PRECIPITATION	3.81	635000.0
RUNOFF	3.029	504851.2
LATERAL DRAINAGE FROM LAYER 2	0.0066	1100.8
PERCOLATION FROM LAYER 3	0.0000	0.1
HEAD ON LAYER 3	36.3	
PERCOLATION FROM LAYER 6	0.00	0.0
SNOW WATER	1.42	236666.7
MAXIMUM VEG. SOIL WATER (VOL/VOL)	0.5010	

MINIMUM VEG. SOIL WATER (VOL/VOL) 0.1351

FINAL WATER STORAGE AT END OF YEAR 78

LAYER	(INCHES)	(VOL/VOL)
----	-----	-----
1	7.36	0.3068
2	3.81	0.3178
3	10.32	0.4300
4	3.94	0.1642
5	10.45	0.1451
6	0.51	0.0842

SNOW WATER 0.00

APPENDIX C

**EXAMPLE OUTPUT FROM
MINTEQA2**

MINTEQ SCENARIO NEAR COVE DURING EARLY PERIOD OF LANDFILL
(High ionic strength, low pH and low pE)

PC VERSION: MINTEQA2
Naval Amphibious Base, Little Creek
Site 7 Landfill

File name = REP1.out

pH = 5.5
pE = -3.4

Temperature (Celsius): 20.00
Units of concentration: MOLAL
Ionic strength: 0.530 molal; FIXED
If specified, total carbonate concentration represents total inorganic carbon.
Do not automatically terminate if charge imbalance exceeds 30%
Precipitation is allowed for all solids in the thermodynamic database and
the print option for solids is set to: 1
The maximum number of iterations is: 40
The method used to compute activity coefficients is: Debye-Huckel equation
Print the full species database including gram-formula weights and Debye-Huckel
parameters.

ID	CONC	K
180	0.300E+00	-0.52
360	0.500E-04	-4.30
500	0.300E+00	-0.52
150	0.100E-01	-2.00
140	0.100E-01	-2.00
730	0.100E+00	-1.00
330	0.316E-05	-5.50
1	0.251E+04	3.40

S(0) HAS BEEN INSERTED FOR POLYSULFIDE CALCULATIONS

H2O HAS BEEN INSERTED AS A COMPONENT

3 2
1 -3.4000 0.0000
330 5.5000 0.0000

S(0) HAS AN ACTIVITY OF 1 AND IS TYPE 3

INPUT DATA BEFORE TYPE MODIFICATIONS

ID	NAME	ACTIVITY GUESS	LOG GUESS	ANAL TOTAL
180	Cl-1	3.020E-01	-0.520	3.000E-01
360	Hg2+2	5.012E-05	-4.300	5.000E-05
500	Na+1	3.020E-01	-0.520	3.000E-01
150	Ca+2	1.000E-02	-2.000	1.000E-02
140	CO3-2	1.000E-02	-2.000	1.000E-02
730	HS-1	1.000E-01	-1.000	1.000E-01
330	H+1	3.162E-06	-5.500	3.162E-06
1	E-1	2.512E+03	3.400	2.512E+03
731	S	1.000E+00	0.000	0.000E-01
2	H2O	1.000E+00	0.000	0.000E-01

Saturation indices and stoichiometry of all minerals

ID #	NAME	Sat. Index	Stoichiometry (in parentheses) of each component
5015000	ARAGONITE	-2.025	(1.000)150 (1.000)140
5015001	CALCITE	-1.871	(1.000)150 (1.000)140
4150000	HALITE	-2.972	(1.000)500 (1.000)180
3050000	NATRON	-7.761	(2.000)500 (1.000)140 (10.000) 2
5050001	THERMONATR	-9.313	(2.000)500 (1.000)140 (1.000) 2
73100	SULFUR	-1.723	(1.000)730 (-1.000)330 (-2.000) 1
2015000	LIME	-24.909	(-2.000)330 (1.000)150 (1.000) 2
2015001	PORTLANDITE	-14.606	(-2.000)330 (1.000)150 (2.000) 2
36000	Hg metal (l	0.000	(0.500)360 (1.000) 1
5036000	Hg2CO3	-28.046	(1.000)360 (1.000)140
4136000	Calomel	-17.533	(1.000)360 (2.000)180
2036000	Hg2(OH)2	-28.495	(1.000)360 (2.000) 2 (-2.000)330
1036000	Hg2S	-19.304	(1.000)360 (1.000)730 (-1.000)330

MINTEQ SCENARIO NEAR COVE DURING LATE PERIOD OF LANDFILL
(High ionic strength, higher pH and low pE)

PC VERSION: MINTEQA2
Naval Amphibious Base, Little Creek
Site 7 Landfill

File name = REP2.out

pH = 7.5
pE = -3.4

Temperature (Celsius): 20.00
Units of concentration: MOLAL
Ionic strength: 0.530 molal; FIXED
If specified, total carbonate concentration represents total inorganic carbon.
Do not automatically terminate if charge imbalance exceeds 30%
Precipitation is allowed for all solids in the thermodynamic database and
the print option for solids is set to: 1
The maximum number of iterations is: 40
The method used to compute activity coefficients is: Debye-Huckel equation
Print the full species database including gram-formula weights and Debye-Huckel
parameters.

ID	CONC	K
180	0.300E+00	-0.52
360	0.500E-04	-4.30
500	0.300E+00	-0.52
150	0.100E-01	-2.00
140	0.100E-01	-2.00
730	0.100E+00	-1.00
330	0.316E-07	-7.50
1	0.251E+04	3.40

S(0) HAS BEEN INSERTED FOR POLYSULFIDE CALCULATIONS

H2O HAS BEEN INSERTED AS A COMPONENT

3 2
1 -3.4000 0.0000
330 7.5000 0.0000

S(0) HAS AN ACTIVITY OF 1 AND IS TYPE 3

INPUT DATA BEFORE TYPE MODIFICATIONS

ID	NAME	ACTIVITY GUESS	LOG GUESS	ANAL TOTAL
180	Cl-1	3.020E-01	-0.520	3.000E-01
360	Hg2+2	5.012E-05	-4.300	5.000E-05
500	Na+1	3.020E-01	-0.520	3.000E-01
150	Ca+2	1.000E-02	-2.000	1.000E-02
140	CO3-2	1.000E-02	-2.000	1.000E-02
730	HS-1	1.000E-01	-1.000	1.000E-01
330	H+1	3.162E-08	-7.500	3.162E-08
1	E-1	2.512E+03	3.400	2.512E+03
731	S	1.000E+00	0.000	0.000E-01
2	H2O	1.000E+00	0.000	0.000E-01

Saturation indices and stoichiometry of all minerals

ID #	NAME	Sat. Index	Stoichiometry (in parentheses) of each component
5015000	ARAGONITE	-0.154	(1.000)150 (1.000)140
5015001	CALCITE	0.000	(1.000)150 (1.000)140
4150000	HALITE	-2.973	(1.000)500 (1.000)180
3050000	NATRON	-5.472	(2.000)500 (1.000)140 (10.000) 2
5050001	THERMONATR	-7.024	(2.000)500 (1.000)140 (1.000) 2
73100	SULFUR	0.000	(1.000)730 (-1.000)330 (-2.000) 1
2015000	LIME	-21.327	(-2.000)330 (1.000)150 (1.000) 2
2015001	PORTLANDITE	-11.024	(-2.000)330 (1.000)150 (2.000) 2
36000	Hg metal (l	0.000	(0.500)360 (1.000) 1
5036000	Hg2CO3	-25.757	(1.000)360 (1.000)140
4136000	Calomel	-17.533	(1.000)360 (2.000)180
2036000	Hg2(OH)2	-24.495	(1.000)360 (2.000) 2 (-2.000)330
1036000	Hg2S	-17.581	(1.000)360 (1.000)730 (-1.000)330

APPENDIX D

HYDROCARBON SPILL SIMULATION MODEL INPUT PARAMETERS

HSSM HYDROCARBON SPILL SIMULATION MODEL

KOPT KINEMATIC OILY POLLUTANT TRANSPORT
OILENS RADIAL OIL LENS MOTION
TSGPLUME TRANSIENT SOURCE GAUSSIAN PLUME

Naval Amphibious Base, Little Creek, VA
Site 7 Landfill
LNAPL SIMULATION

INPUT DATA

=====

CONSTANTS & MATRIX PROPERTIES.....
SAT. VERT. HYD.CONDUCTIVITY = 5.000
RATIO OF HORIZONTA TO
VERTICAL CONDUCTIVITY = 10.00
RELATIVE PERMEABILITY INDEX = 1
POROSITY = .3000
RESIDUAL WATER SATURATION = .4000E-01
BROOKS AND COREY'S LAMBDA = .8000

WATER EVENT CHARACTERISTICS.....
DYNAMIC VISCOSITY = 1.000
DENSITY = 1.000
RAIN TYPE : 1-FLUX 2-SAT. = 1
WATER FLUX OR SATURATION = .7000E-03
MAX KRW DURING INFILTRATION = .5000
DEPTH TO WATER TABLE = 1.000

POLLUTANT EVENT CHARACTERISTICS.....
DYNAMIC VISCOSITY = 4.000
DENSITY = .7500
RESIDUAL OIL SATURATION = .1000
OIL LOADING TYPE = 1

CAPILLARY SUCTION PARAMETERS.....
AIR ENTRY HEAD = .5000E-01
WATER SURFACE TENSION = 65.00
OIL SURFACE TENSION = 35.00

FLUX LOADING RATE = .5000E-01
BEGINNING TIME = .0000
ENDING TIME = 3.000

DISSOLVED CONSTITUENT PARAMETERS.....

INITIAL CONC. IN OIL = 8000.
OIL/WATER PARTITION COEF. = 300.0
SOIL/WATER PARTITION COEF. = .8300
SOIL/WATER (HYDROCARBON) = .8300
BULK DENSITY = 1.600

OILENS SUBMODEL PARAMETERS.....

RADIUS OF POLLUTANT SOURCE = 20.00
RADIUS MULTIPLYING FACTOR = 1.001
THICKNESS OF CAP. FRINGE = .2500
AQUIFER'S VERT DISPERSIVITY = .1000
GROUNDWATER GRADIENT = .1800E-02
OIL RESIDUAL IN AQUIFER = .2000
MAX OIL SATURATION IN LENS = .5000
WATER SOLUBILITY CONTAMINANT= 1780.
WATER SOLUBILITY OF OIL = 32.00

SIMULATION PARAMETERS.....

SIMULATION ENDING TIME = .2500E+05
MAXIMUM RKF TIME STEP = 5.000
MIN. TIME BETWEEN PRINTING = .2500
ENDING CRITERIA = 4
FACTOR FOR ENDING CRITERIA 4= .2000E-01

PROFILES.....

NUMBER OF PROFILES = 4
AT TIMES:
365.0000 1000.0000 3650.0000
10000.0000

TSGPLUME MODEL PARAMETERS.....

LONGITUDINAL DISPERSIVITY (M) 10.00
TRANSVERSE DISPERSIVITY (M) 2.000
PERCENT MAX. RADIUS 100.0
MINIMUM OUTPUT CONC. (MG/L) .1000E-01
CONSTITUENT HALF LIFE (D) 1000.
NUMBER OF RECEPTOR WELLS 1
BEGINNING TIME (D) 100.0
ENDING TIME (D) .1000E+05

TIME INCREMENT (D) 100.0
AQUIFER THICKNESS (M) 3.000

RECEPTOR WELL LOCATIONS

X	Y
230.0	.0000

END OF INPUT DATA

CALCULATED PARAMETERS.....

SAT. OIL CONDUCTIVITY = .9375
AREA OF THE SOURCE = 1257.
OIL DECAY RATE = .6931E-03
TRAPPED AIR SATURATION = .1137
WATER SATURATION = .2312
WATER FLUX = .7000E-03
MAX. OIL CONDUCTIVITY = .2282
POLLUANT VOLUME FLUX = .5000E-01
TOTAL OIL LOADING, VOL/AREA = .1500
TOTAL OIL MASS (KG) = .1414E+06
TOTAL CONSTITUENT LOADING = 1.200

APPENDIX E

SAMPLE UNMOC PROGRAM INPUT FILE

```

15 1 20 28 0 0 0 0 0 9 0 7 200
1 1 0 0 0 0
365 0.01 0.30 10. 0.15 22. 26. 0.33 0.5 1.0
0 335
0 7.0
0 -6.0
0 0.0
0 0.0
0 0.0
0 0.0

```

141

1 10.0 0.0 2.4 0.0 0.0
 2 10.0 0.0 1.0 0.0 0.0
 3 0.0 0.0 0.0 0.0 -0.0007
 4 0.0 0.0 0.0 0.0 -0.0007
 5 0.0 0.0 0.0 0.0 -0.0007
 6 0.0 0.0 0.0 0.0 -0.0007
 7 0.0 0.0 0.0 0.0 -0.0007
 8 0.0 0.0 0.0 0.0 -0.0007
 9 0.0 0.0 0.0 0.0 -0.0007

1 0 0 0 200 1 0 1034
 1 10.0 0.0 2.4 0.0 0.0
 2 10.0 0.0 1.0 0.0 0.0
 3 0.0 0.0 0.0 0.0 -0.0007
 4 0.0 67500 0.0 0.0 -0.0007
 5 0.0 0.0 0.0 0.0 -0.0007
 6 0.0 0.0 0.0 0.0 -0.0007
 7 0.0 0.0 0.0 0.0 -0.0007
 8 0.0 0.0 0.0 0.0 -0.0007
 9 0.0 0.0 0.0 0.0 -0.0007

1 0 0 0 200 1 0 1034
 1 10.0 0.0 2.4 0.0 0.0
 2 10.0 0.0 1.0 0.0 0.0
 3 0.0 0.0 0.0 0.0 -0.0007
 4 0.0 47500 0.0 0.0 -0.0007
 5 0.0 67500 0.0 0.0 -0.0007
 6 0.0 0.0 0.0 0.0 -0.0007
 7 0.0 0.0 0.0 0.0 -0.0007
 8 0.0 0.0 0.0 0.0 -0.0007
 9 0.0 0.0 0.0 0.0 -0.0007

1 0 0 0 200 1 0 1034
 1 10.0 0.0 2.4 0.0 0.0
 2 10.0 0.0 1.0 0.0 0.0
 3 0.0 0.0 0.0 0.0 -0.0007
 4 0.0 36000 0.0 0.0 -0.0007
 5 0.0 47500 0.0 0.0 -0.0007
 6 0.0 67500 0.0 0.0 -0.0007
 7 0.0 0.0 0.0 0.0 -0.0007
 8 0.0 0.0 0.0 0.0 -0.0007
 9 0.0 0.0 0.0 0.0 -0.0007

1 0 0 0 200 1 0 1034
 1 10.0 0.0 2.4 0.0 0.0
 2 10.0 0.0 1.0 0.0 0.0
 3 0.0 0.0 0.0 0.0 -0.0007
 4 0.0 30000 0.0 0.0 -0.0007
 5 0.0 40000 0.0 0.0 -0.0007
 6 0.0 50000 0.0 0.0 -0.0007
 7 0.0 70000 0.0 0.0 -0.0007
 8 0.0 0.0 0.0 0.0 -0.0007
 9 0.0 0.0 0.0 0.0 -0.0007

1 0 0 0 200 1 0 1034
 1 10.0 0.0 2.4 0.0 0.0
 2 10.0 0.0 1.0 0.0 0.0
 3 0.0 0.0 0.0 0.0 -0.0007
 4 0.0 24000 0.0 0.0 -0.0007
 5 0.0 32000 0.0 0.0 -0.0007
 6 0.0 42000 0.0 0.0 -0.0007
 7 0.0 54000 0.0 0.0 -0.0007
 8 0.0 67500 0.0 0.0 -0.0007
 9 0.0 0.0 0.0 0.0 -0.0007

1 0 0 0 200 1 0 1034
 1 10.0 0.0 2.4 0.0 0.0
 2 10.0 0.0 1.0 0.0 0.0
 3 0.0 0.0 0.0 0.0 -0.0007
 4 0.0 19000 0.0 0.0 -0.0007
 5 0.0 21000 0.0 0.0 -0.0007
 6 0.0 28000 0.0 0.0 -0.0007
 7 0.0 42000 0.0 0.0 -0.0007
 8 0.0 47500 0.0 0.0 -0.0007
 9 0.0 67500 0.0 0.0 -0.0007

1 0 0 0 200 1 0 2190
 1 10.0 0.0 2.4 0.0 0.0
 2 10.0 0.0 1.0 0.0 0.0
 3 0.0 0.0 0.0 0.0 -0.0007
 4 0.0 14000 0.0 0.0 -0.0007
 5 0.0 17000 0.0 0.0 -0.0007
 6 0.0 20000 0.0 0.0 -0.0007
 7 0.0 24000 0.0 0.0 -0.0007
 8 0.0 28000 0.0 0.0 -0.0007
 9 0.0 40000 0.0 0.0 -0.0007

1 0 0 0 200 1 0 1825
 1 10.0 0.0 2.4 0.0 0.0
 2 10.0 0.0 1.0 0.0 0.0
 3 0.0 0.0 0.0 0.0 -0.0007
 4 0.0 8500 0.0 0.0 -0.0007
 5 0.0 10000 0.0 0.0 -0.0007
 6 0.0 13000 0.0 0.0 -0.0007
 7 0.0 15000 0.0 0.0 -0.0007
 8 0.0 19000 0.0 0.0 -0.0007
 9 0.0 23000 0.0 0.0 -0.0007

1 0 0 0 200 1 0 1278
 1 10.0 0.0 2.4 0.0 0.0
 2 10.0 0.0 1.0 0.0 0.0
 3 0.0 0.0 0.0 0.0 -0.0007
 4 0.0 6500 0.0 0.0 -0.0007
 5 0.0 8500 0.0 0.0 -0.0007
 6 0.0 9000 0.0 0.0 -0.0007
 7 0.0 11000 0.0 0.0 -0.0007
 8 0.0 14000 0.0 0.0 -0.0007
 9 0.0 19000 0.0 0.0 -0.0007

1 0 0 0 200 1 0 365
 1 10.0 0.0 2.4 0.0 0.0
 2 10.0 0.0 2.5 0.0 0.0
 3 0.0 0.0 0.0 0.0 -0.0007
 4 0.0 6000 0.0 0.0 -0.0007
 5 0.0 8000 0.0 0.0 -0.0007
 6 0.0 8500 0.0 0.0 -0.0007
 7 0.0 10000 0.0 0.0 -0.0007
 8 0.0 12000 0.0 0.0 -0.0007
 9 0.0 17000 0.0 0.0 -0.0007

1 0 0 0 200 1 0 365
 1 10.0 0.0 1.0 0.0 0.0
 2 10.0 0.0 2.5 0.0 0.0
 3 0.0 0.0 0.0 0.0 -0.0007
 4 0.0 6000 0.0 0.0 -0.0007
 5 0.0 8000 0.0 0.0 -0.0007
 6 0.0 8500 0.0 0.0 -0.0007
 7 0.0 10000 0.0 0.0 -0.0007
 8 0.0 12000 0.0 0.0 -0.0007
 9 0.0 17000 0.0 0.0 -0.0007

1 0 0 0 200 1 0 365
 1 10.0 0.0 1.0 0.0 0.0
 2 10.0 0.0 2.5 0.0 0.0
 3 0.0 0.0 0.0 0.0 -0.0007
 4 0.0 5500 0.0 0.0 -0.0007
 5 0.0 7500 0.0 0.0 -0.0007
 6 0.0 8000 0.0 0.0 -0.0007
 7 0.0 9500 0.0 0.0 -0.0007
 8 0.0 11500 0.0 0.0 -0.0007
 9 0.0 16000 0.0 0.0 -0.0007

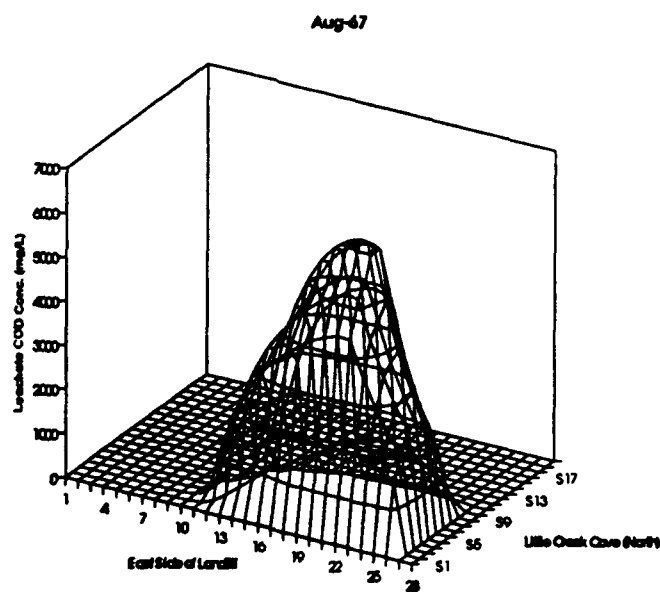
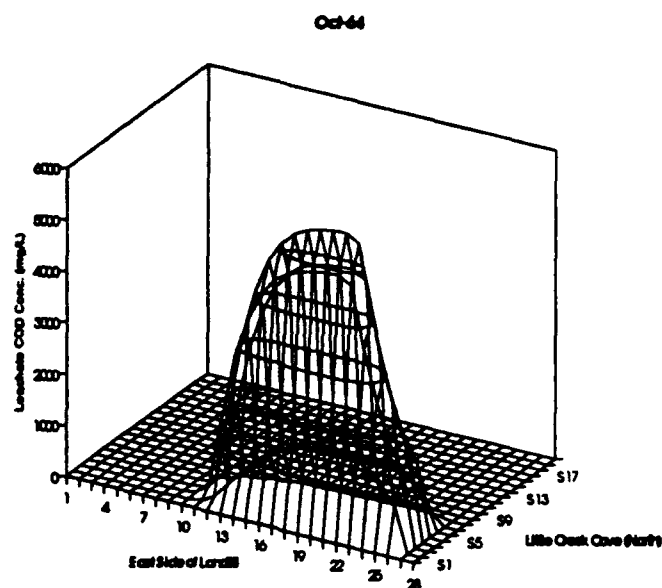
1 0 0 0 200 1 0 365
 1 10.0 0.0 1.0 0.0 0.0
 2 10.0 0.0 2.5 0.0 0.0
 3 0.0 0.0 0.0 0.0 -0.0007
 4 0.0 5500 0.0 0.0 -0.0007
 5 0.0 7500 0.0 0.0 -0.0007
 6 0.0 8500 0.0 0.0 -0.0007
 7 0.0 9000 0.0 0.0 -0.0007
 8 0.0 10000 0.0 0.0 -0.0007
 9 0.0 15000 0.0 0.0 -0.0007

1 0 0 0 200 1 0 365
 1 10.0 0.0 1.0 0.0 0.0
 2 10.0 0.0 2.5 0.0 0.0
 3 0.0 0.0 0.0 0.0 -0.0007
 4 0.0 5500 0.0 0.0 -0.0007
 5 0.0 7500 0.0 0.0 -0.0007
 6 0.0 8000 0.0 0.0 -0.0007
 7 0.0 8500 0.0 0.0 -0.0007
 8 0.0 10000 0.0 0.0 -0.0007
 9 0.0 14000 0.0 0.0 -0.0007

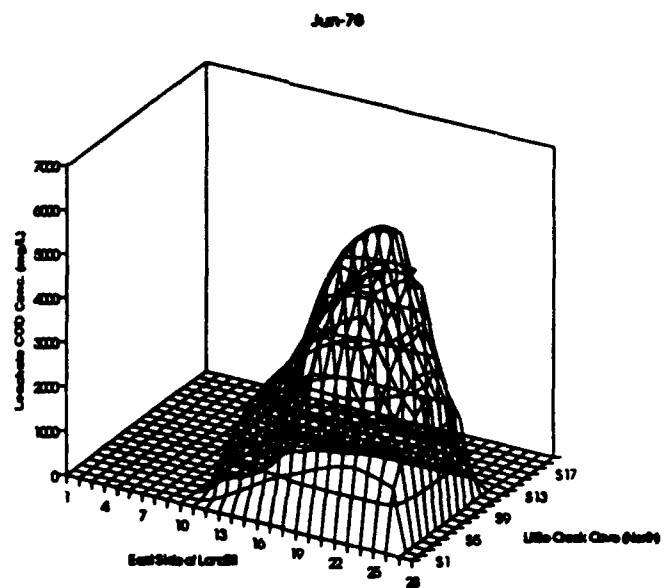
APPENDIX F

ADDITIONAL UNMOC PROGRAM OUTPUT

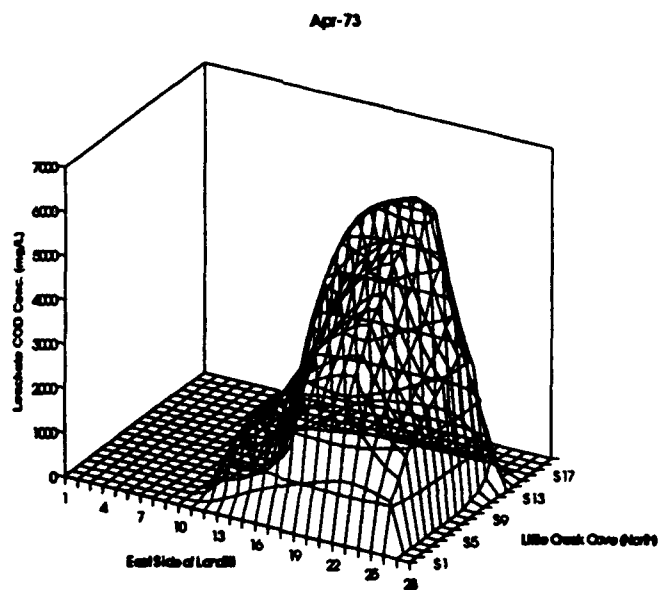
Figures F1 (a) - (b). UNMOC model results for $R_f = 2$, $T_{1/2} = 1,000d$ and $K = 33.5 m/d$.



Figures F1 (c) - (c). UNMOC model results for $R_f = 2$, $T_{1/2} = 1,000d$ and $K = 33.5 \text{ m/d}$.

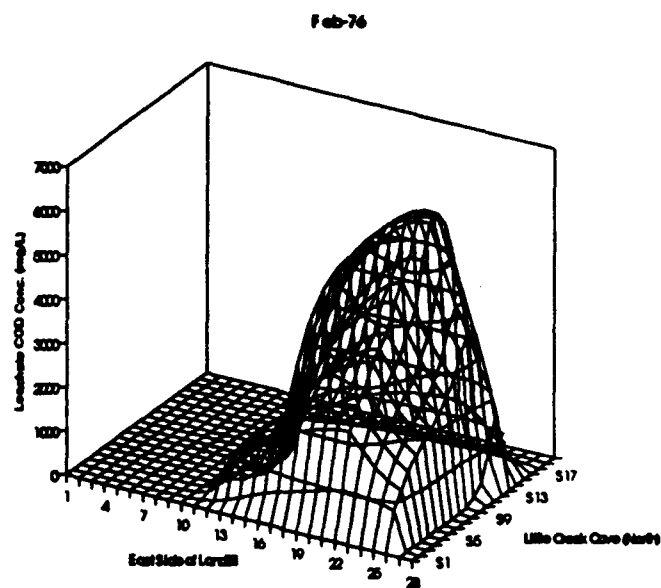


(c)

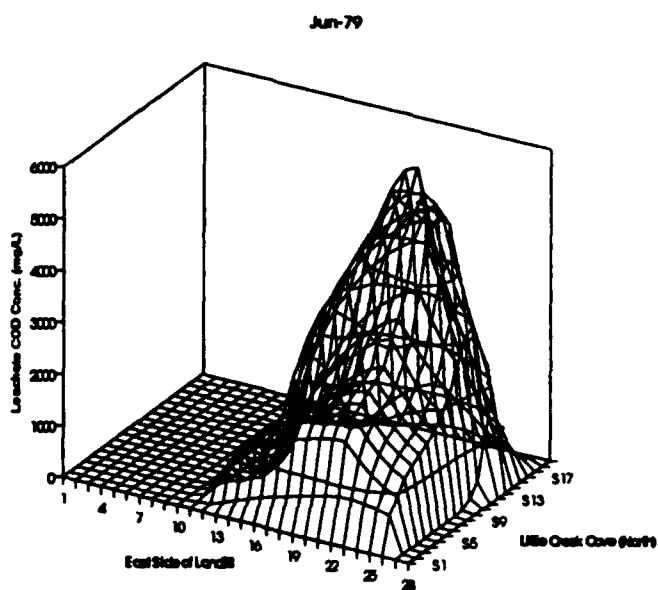


(d)

Figures F1 (e) - (f). UNMOC model results for $R_f = 2$, $T_{1/2} = 1,000d$ and $K = 33.5 \text{ m/d}$.

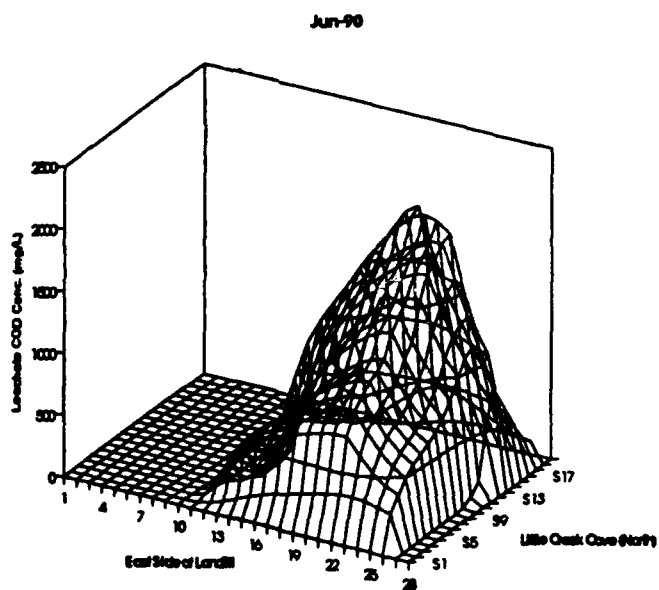
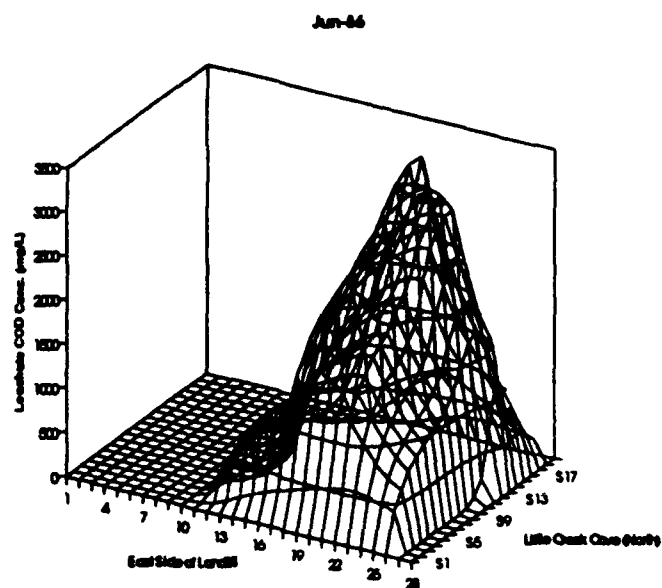


(e)

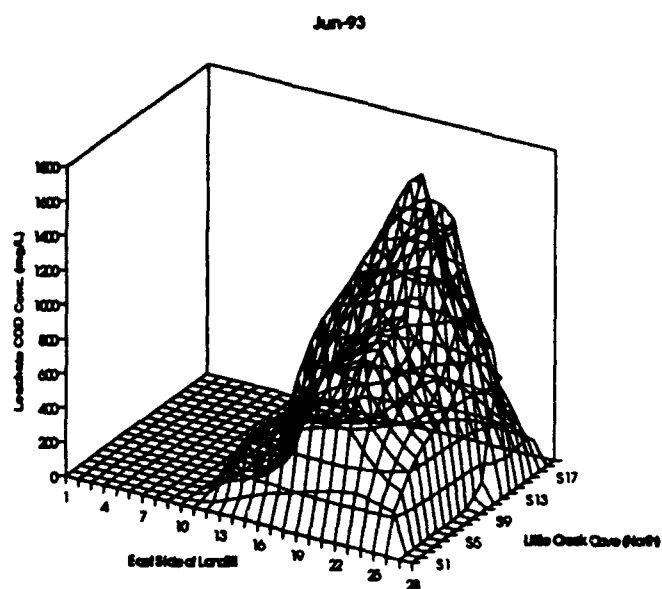


(f)

Figures F1 (g) - (h). UNMOC model results for $R_f = 2$, $T_{1/2} = 1,000d$ and $K = 33.5 \text{ m/d}$.

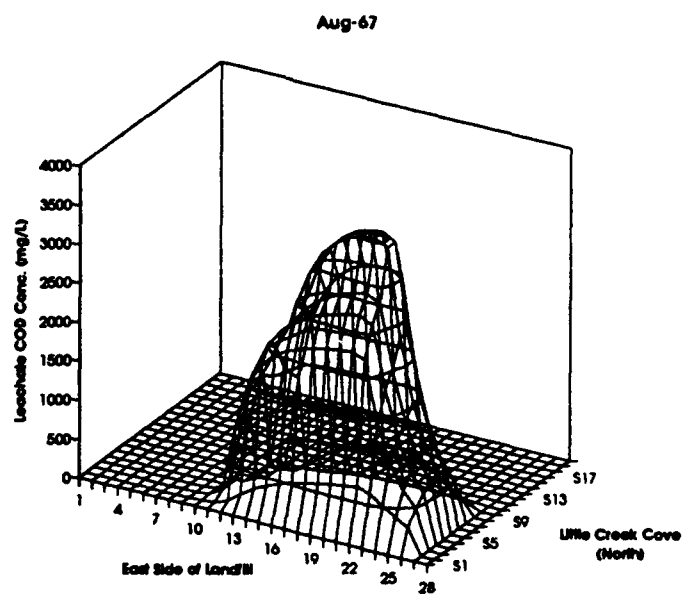
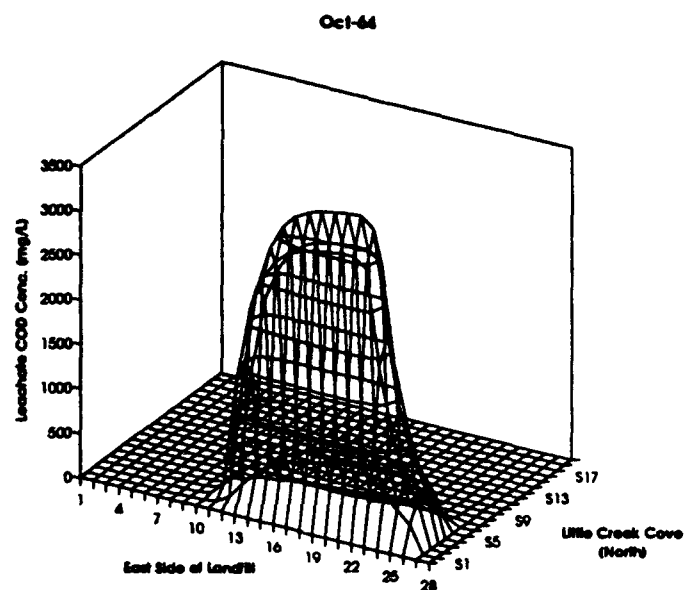


Figures F1 (i). UNMOC model results for $R_f = 2$, $T_{1/2} = 1,000d$ and $K = 33.5$ m/d.

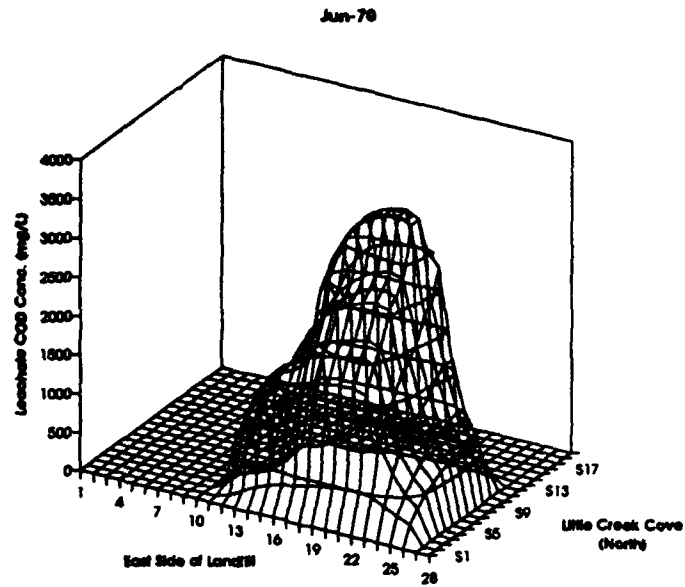


(i)

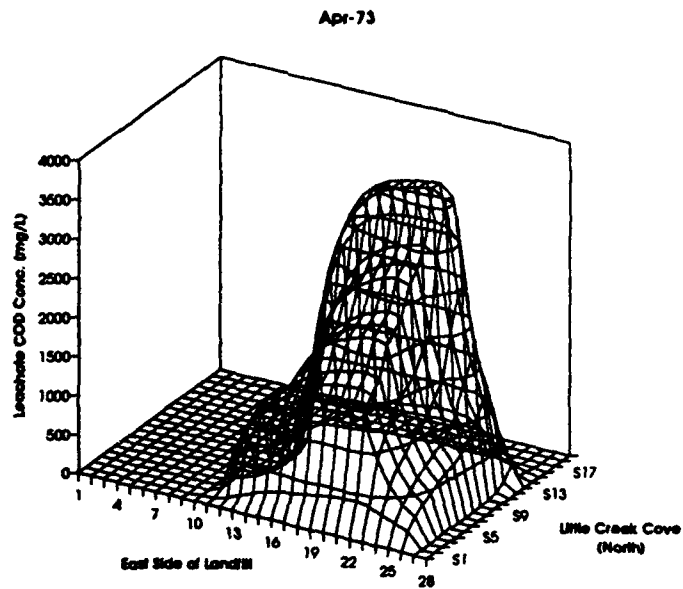
Figures F2 (a) - (b). UNMOC model results for $R_f = 2$, $T_{1/2} = 400d$ and $K = 33.5 \text{ m/d}$.



Figures F2 (c) - (d). UNMOC model results for $R_f = 2$, $T_{1/2} = 400d$ and $K = 33.5 \text{ m/d}$.

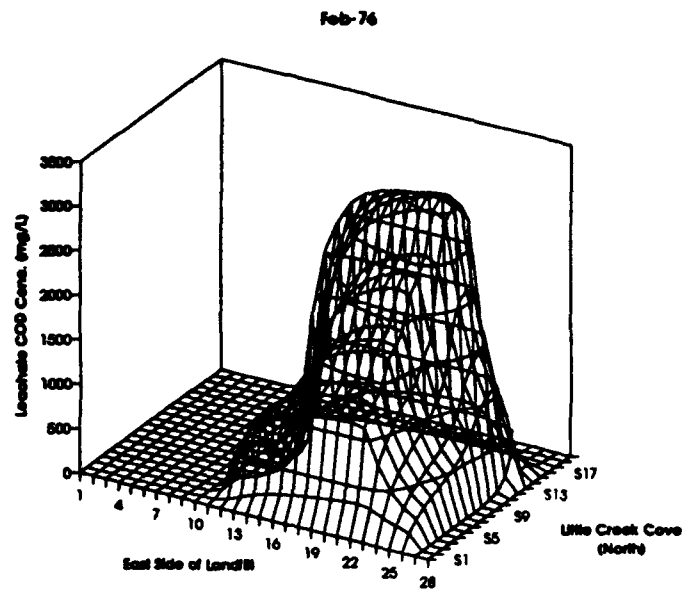


(c)

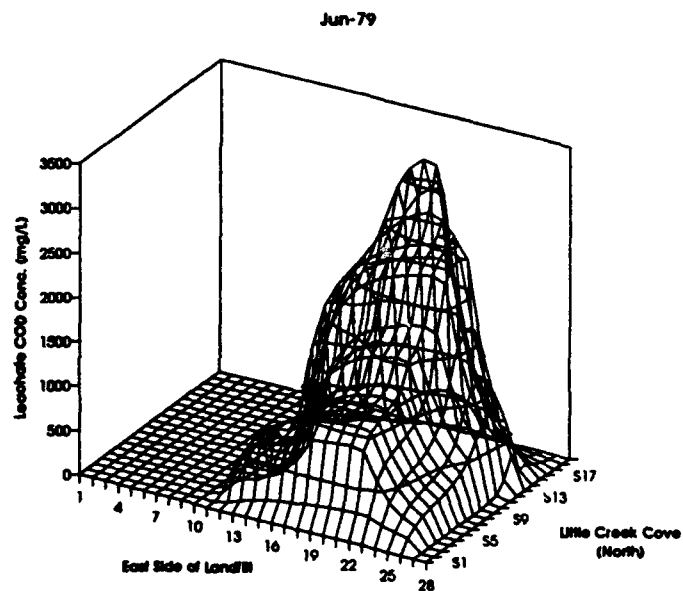


(d)

Figures F2 (e) - (f). UNMOC model results for $R_f = 2$, $T_{1/2} = 400d$ and $K = 33.5 \text{ m/d}$.

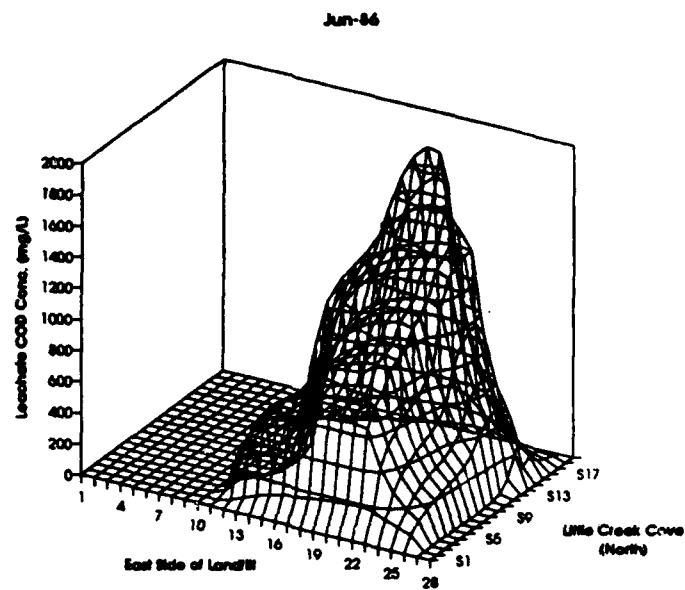


(e)

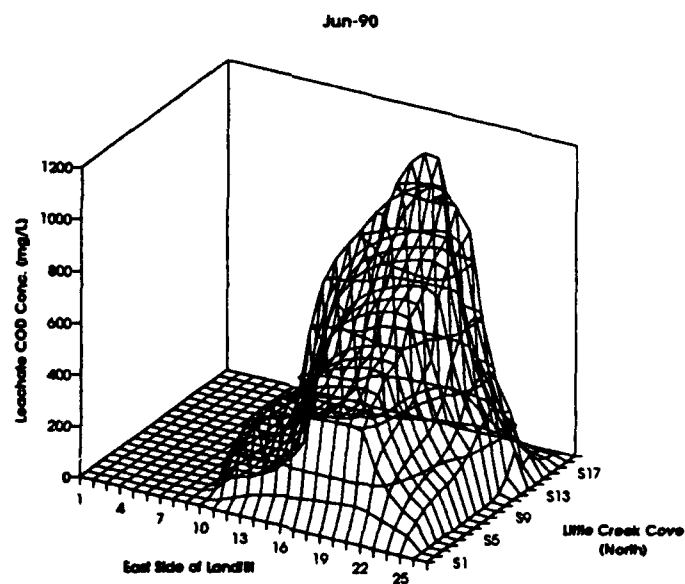


(f)

Figures F2 (g) - (h). UNMOC model results for $R_f = 2$, $T_{1/2} = 400\text{d}$ and $K = 33.5\text{ m/d}$.

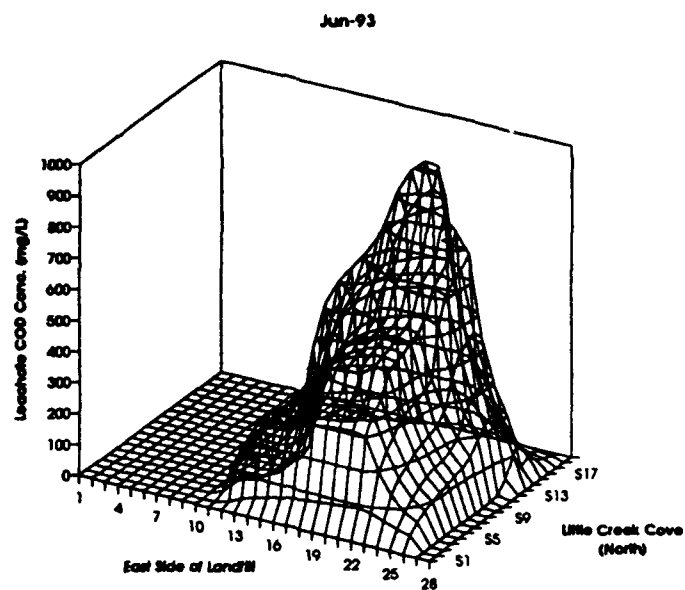


(g)

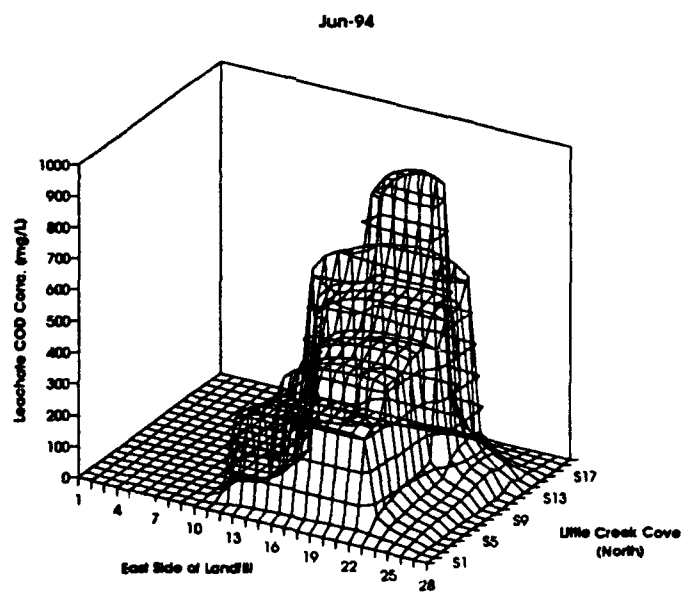


(h)

Figures F2 (i) - (j). UNMOC model results for $R_f = 2$, $T_{1/2} = 400\text{d}$ and $K = 33.5\text{ m/d}$.

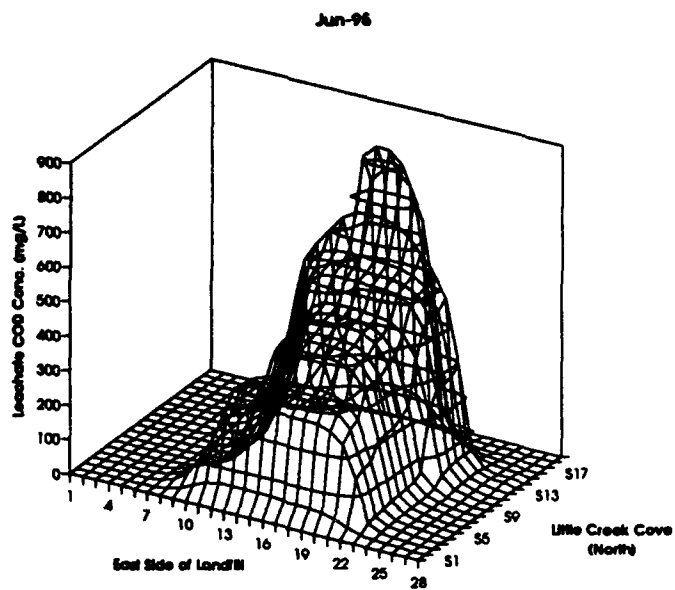


(i)

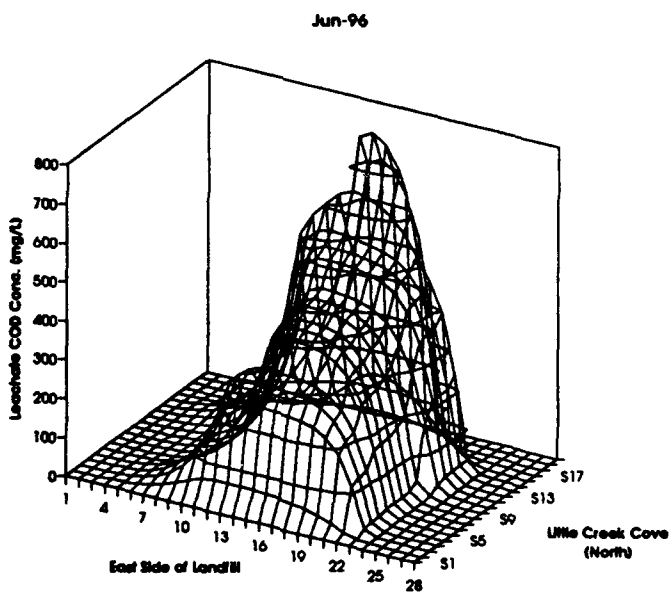


(j)

Figures F2 (k) - (l). UNMOC model results for $R_f = 2$, $T_{1/2} = 400d$ and $K = 33.5$ m/d.

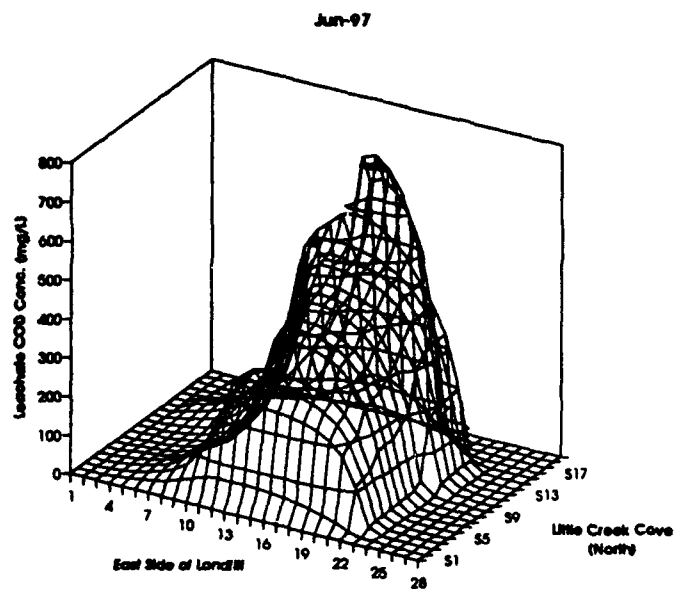


(k)

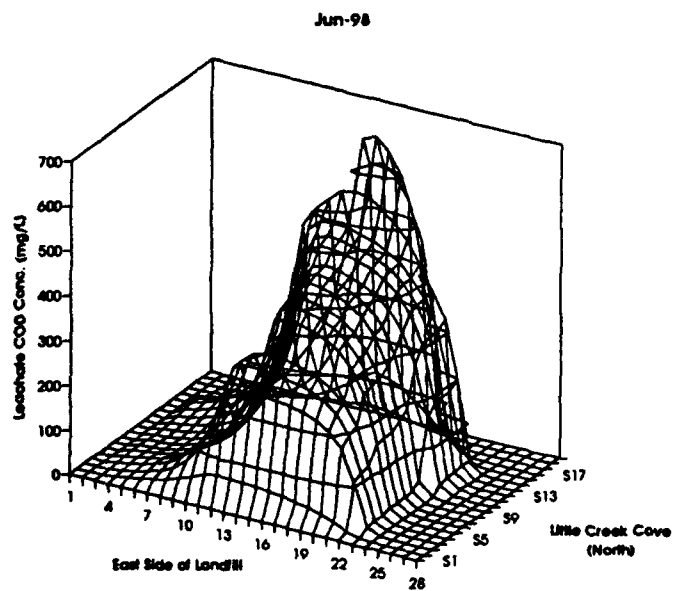


(l)

Figures F2 (m) - (n). UNMOC model results for $R_f = 2$, $T_{1/2} = 400d$ and $K = 33.5 \text{ m/d}$.

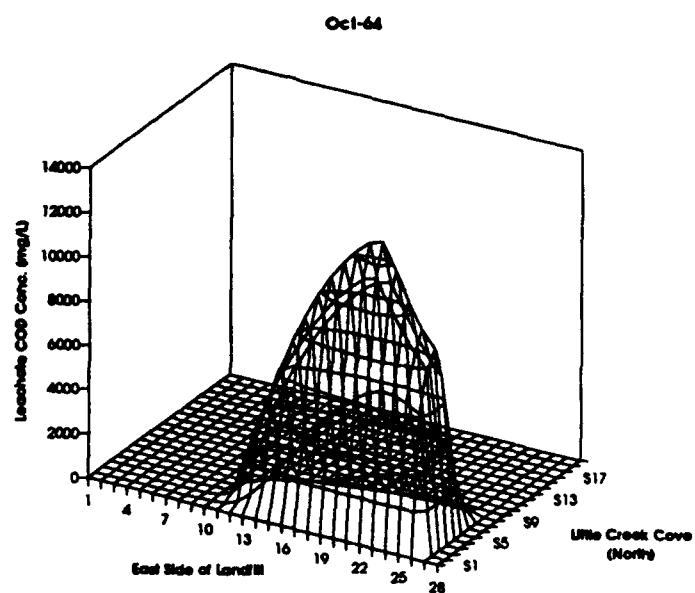


(m)

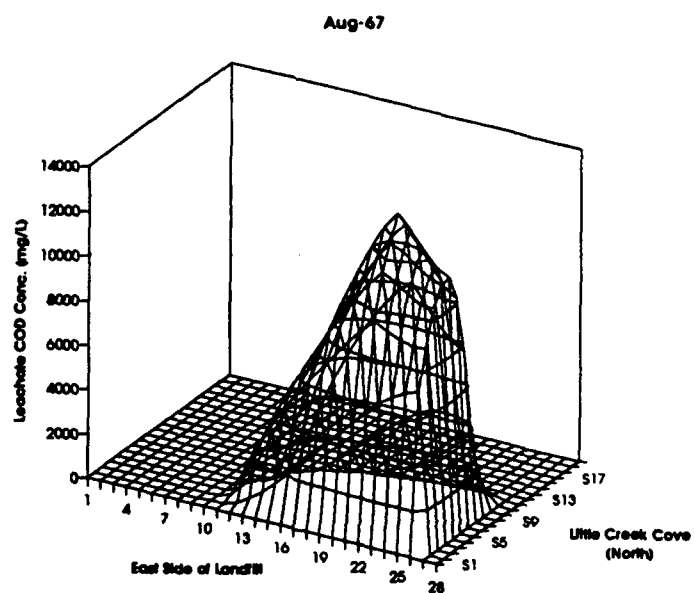


(n)

Figures F3 (a) - (b). UNMOC model results for $R_f = 1$, no degradation and $K = 33.5$ m/d.

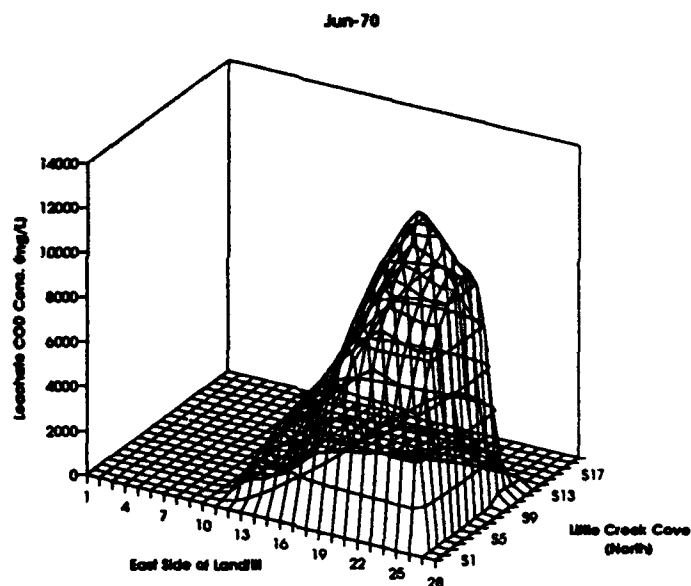


(a)

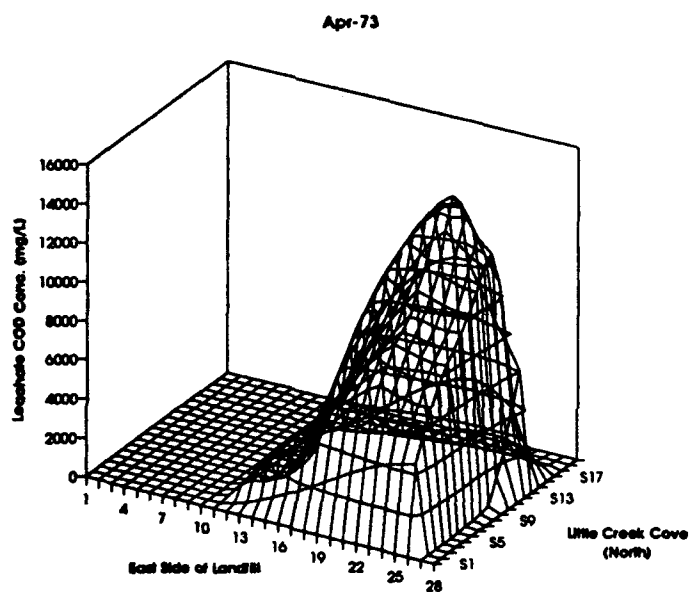


(b)

Figures F3 (c) - (d). UNMOC model results for $R_f = 1$, no degradation and $K = 33.5$ m/d.

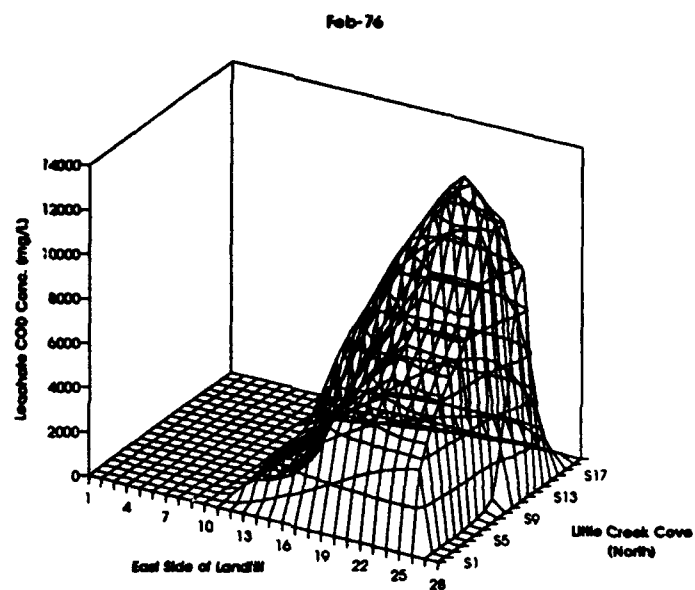


(c)

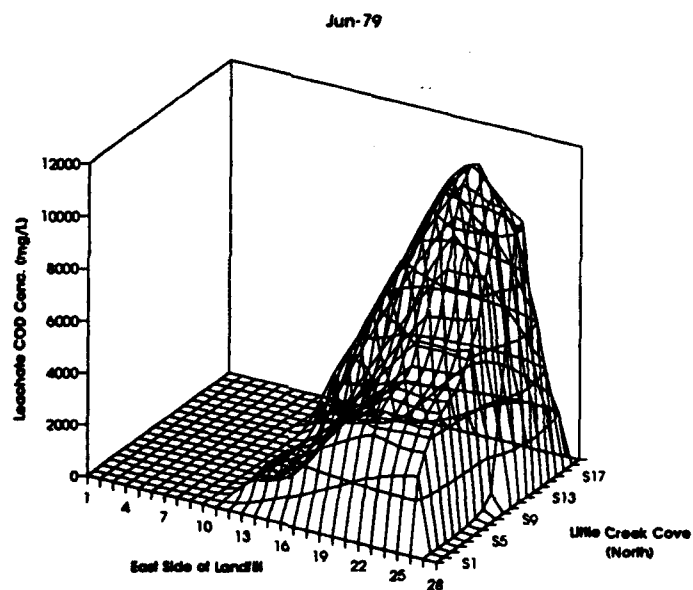


(d)

Figures F3 (e) - (f). UNMOC model results for $R_f = 1$, no degradation and $K = 33.5$ m/d.

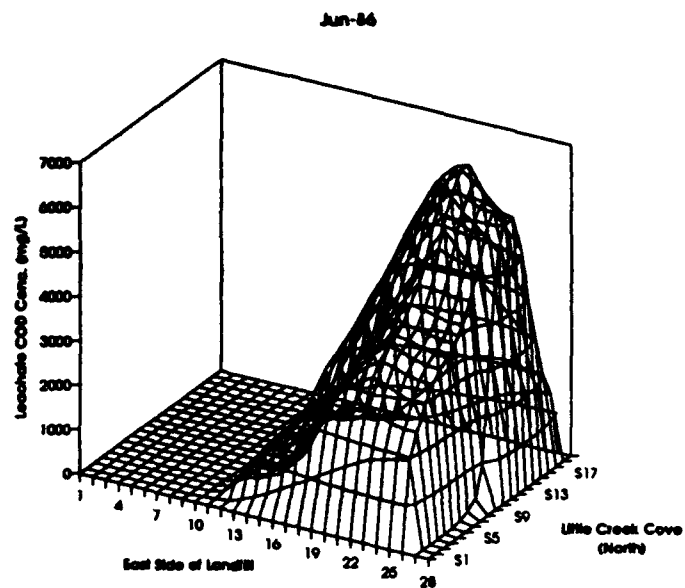


(e)

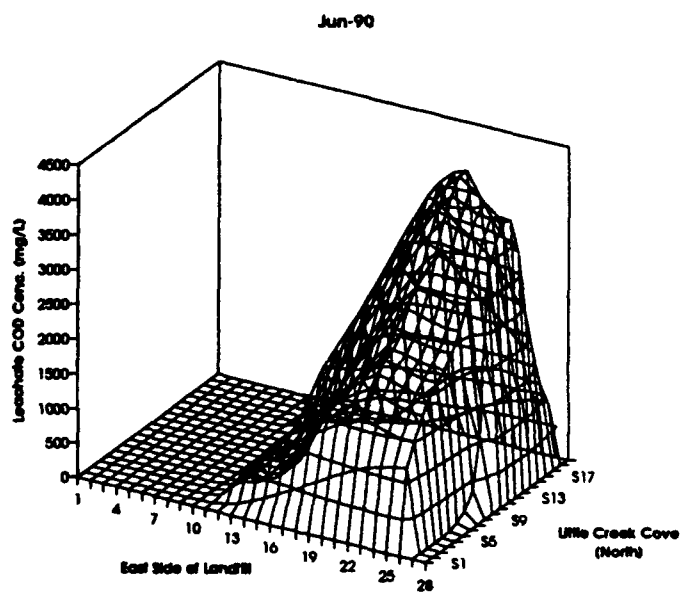


(f)

Figures F3 (g) - (h). UNMOC model results for $R_f = 1$, no degradation and $K = 33.5$ m/d.

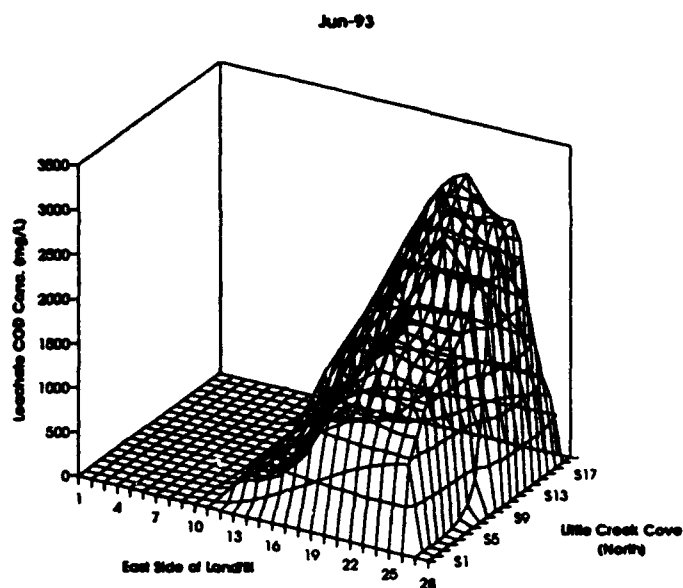


(g)

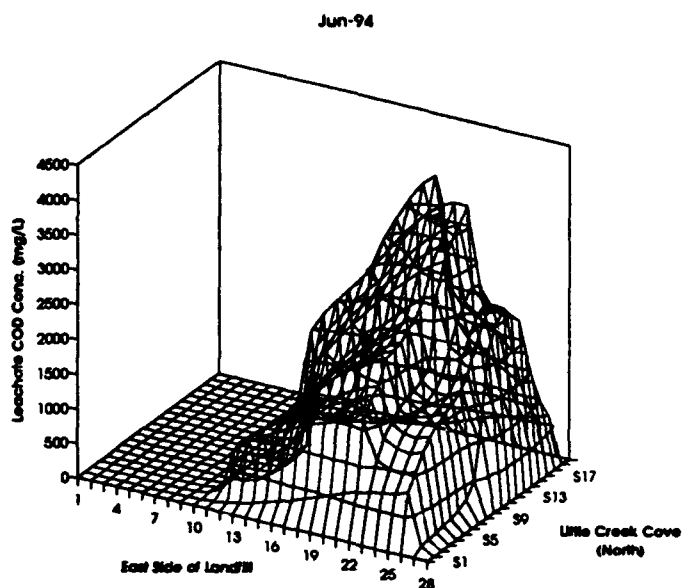


(h)

Figures F3 (i) - (j). UNMOC model results for $R_f = 1$, no degradation and $K = 33.5$ m/d.

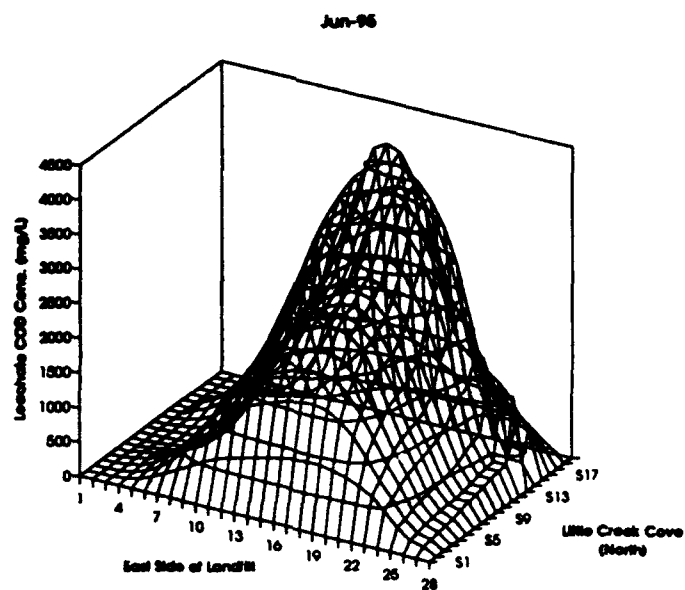


(i)

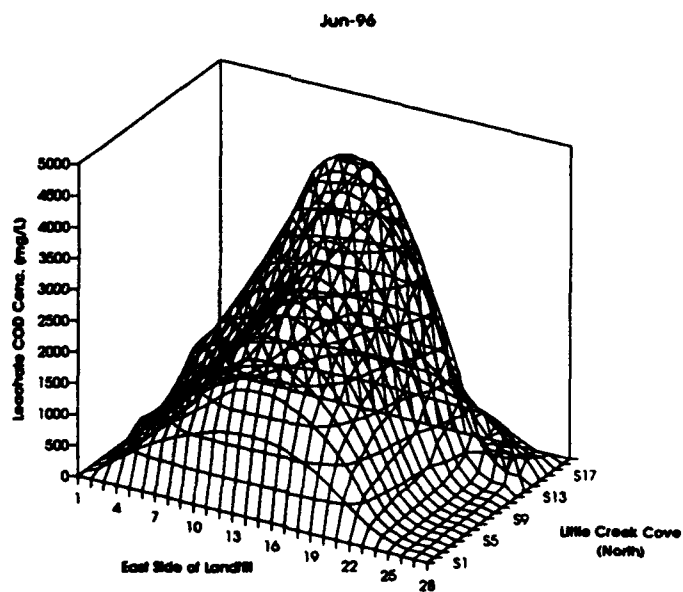


(j)

Figures F3 (k) - (l). UNMOC model results for $R_f = 1$, no degradation and $K = 33.5$ m/d.

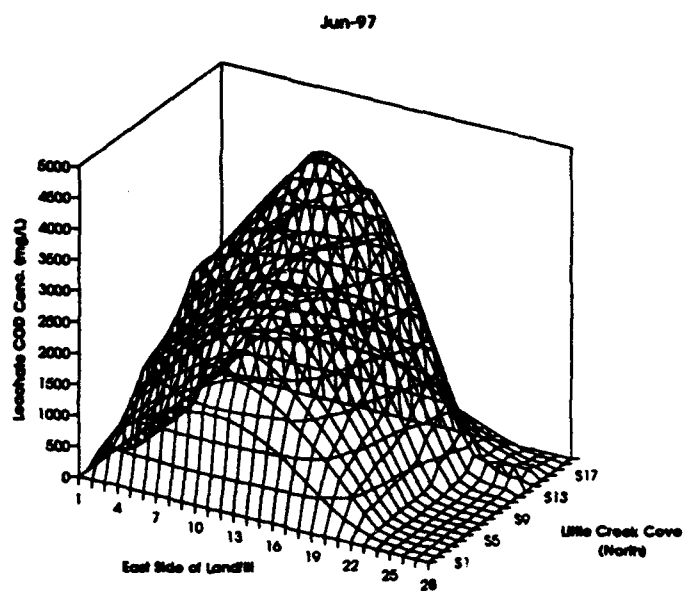


(k)

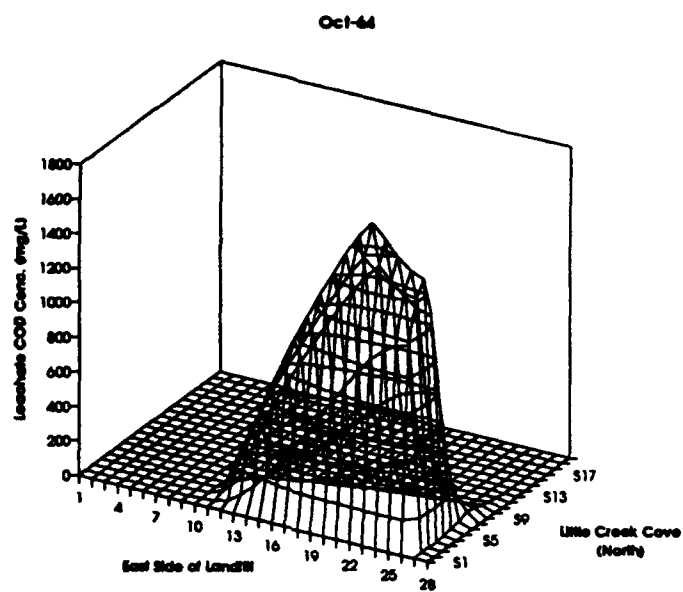


(l)

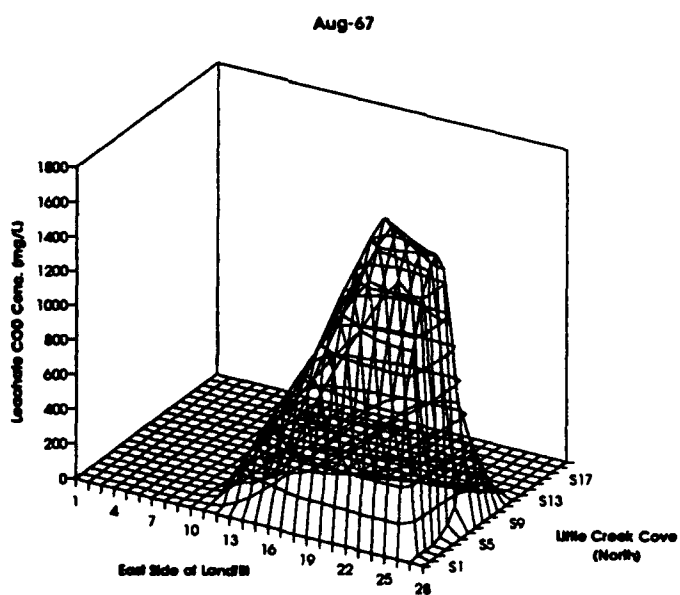
Figures F3 (m). UNMOC model results for $R_f = 1$, no degradation and $K = 33.5$ m/d.



Figures F4(a) - (b). UNMOC model results for $R_f = 1$, no degradation and $K = 335$ m/d.

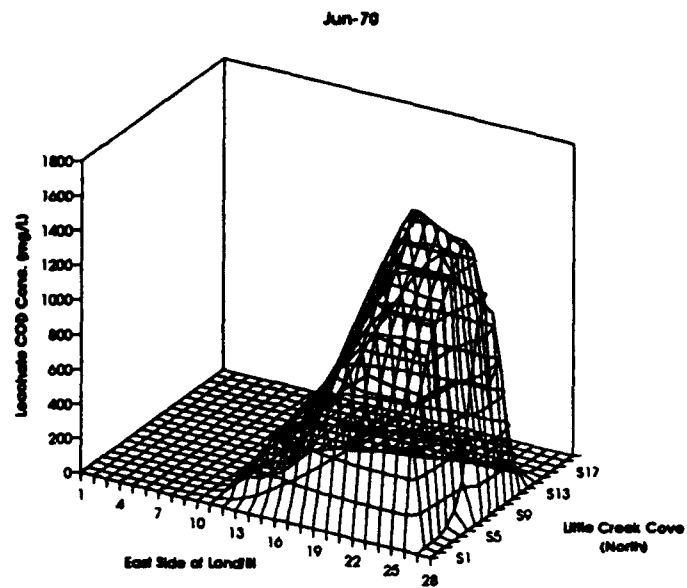


(a)

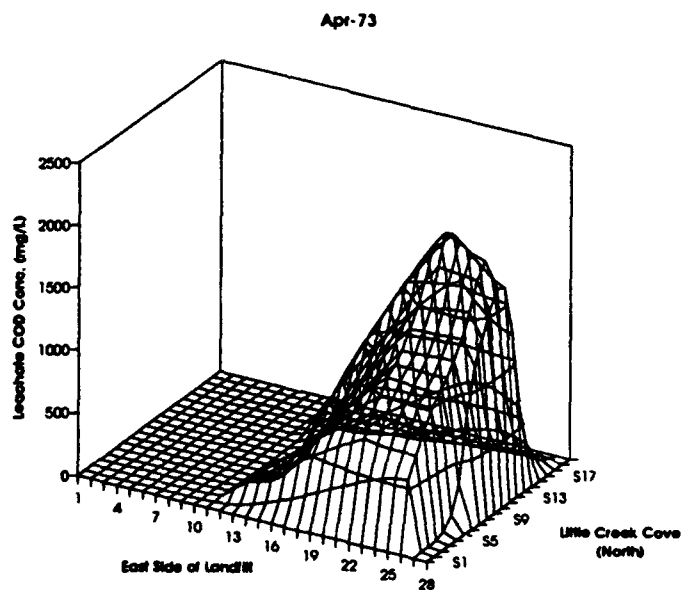


(b)

Figures F4(c) - (d). UNMOC model results for $R_f = 1$, no degradation and $K = 335$ m/d.

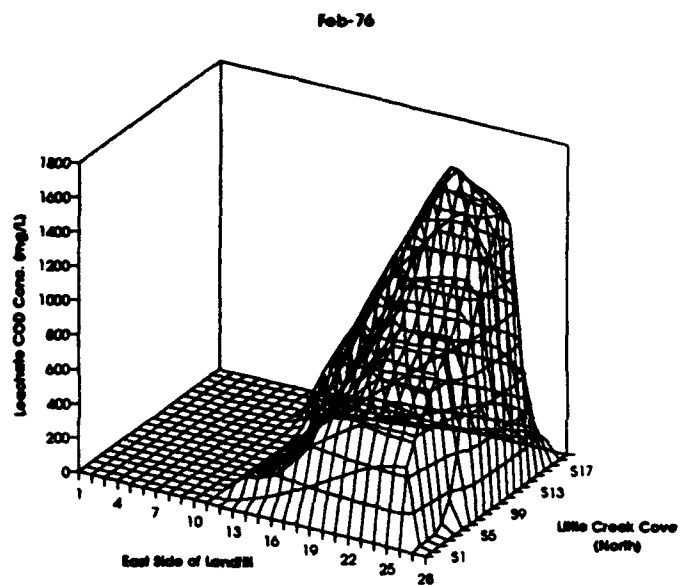


(c)

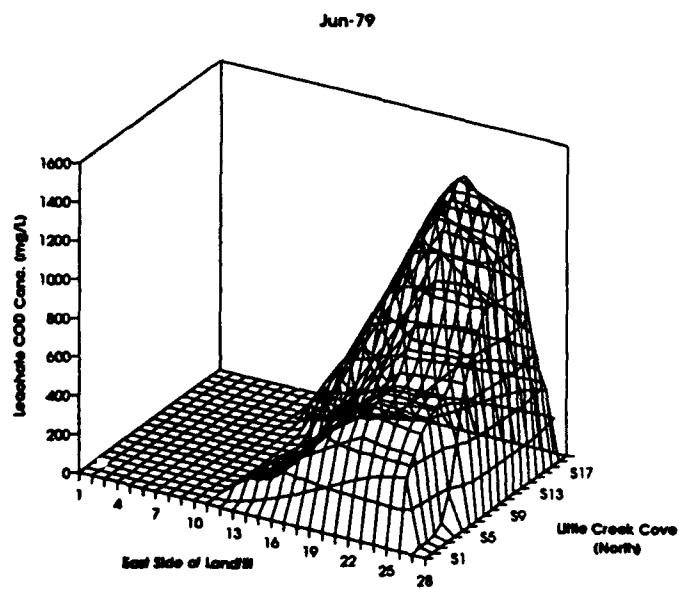


(d)

Figures F4(e) - (f). UNMOC model results for $R_f = 1$, no degradation and $K = 335$ m/d.

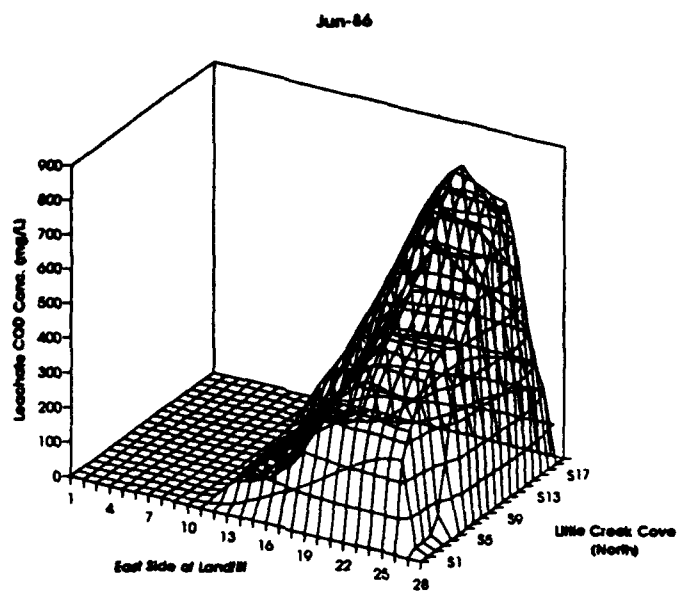


(e)

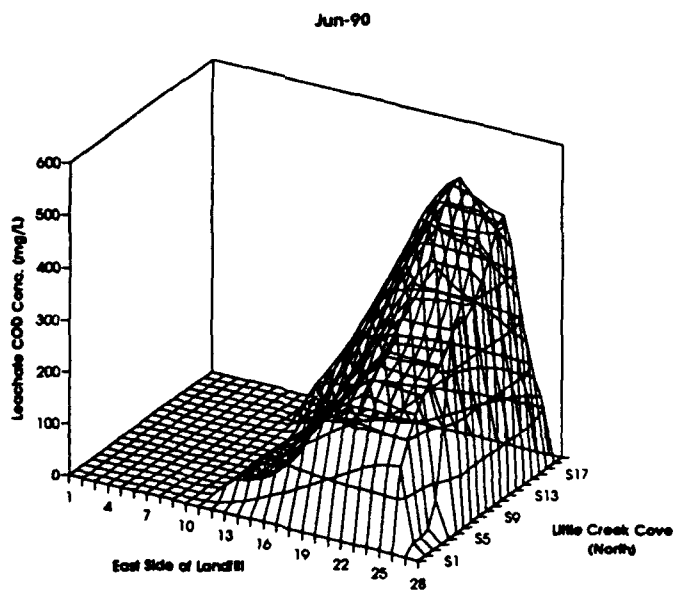


(f)

Figures F4(g) - (h). UNMOC model results for $R_f = 1$, no degradation and $K = 335$ m/d.

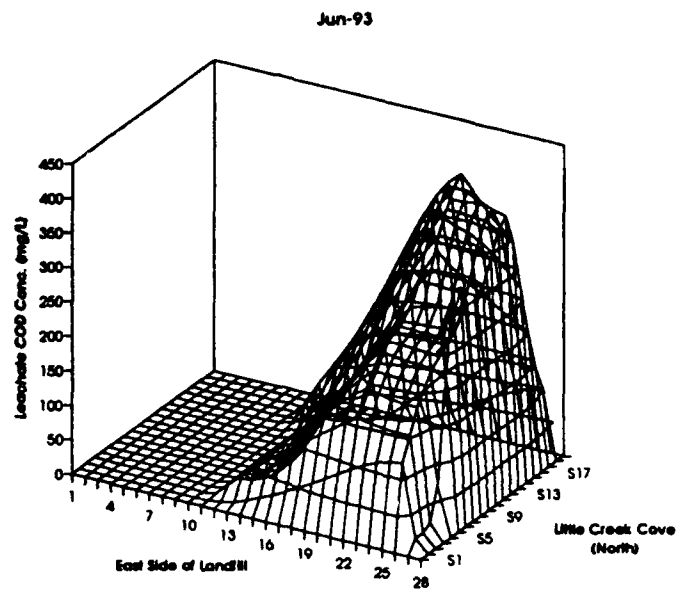


(g)

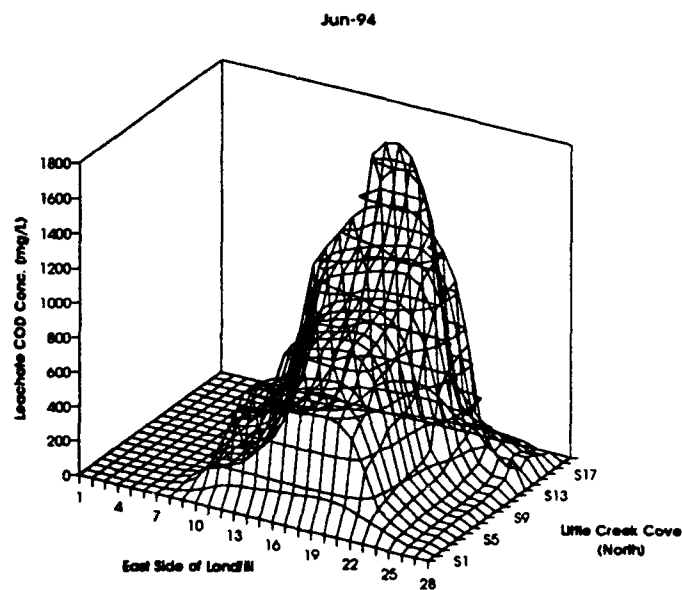


(h)

Figures F4(i) - (j). UNMOC model results for $R_f = 1$, no degradation and $K = 335$ m/d.

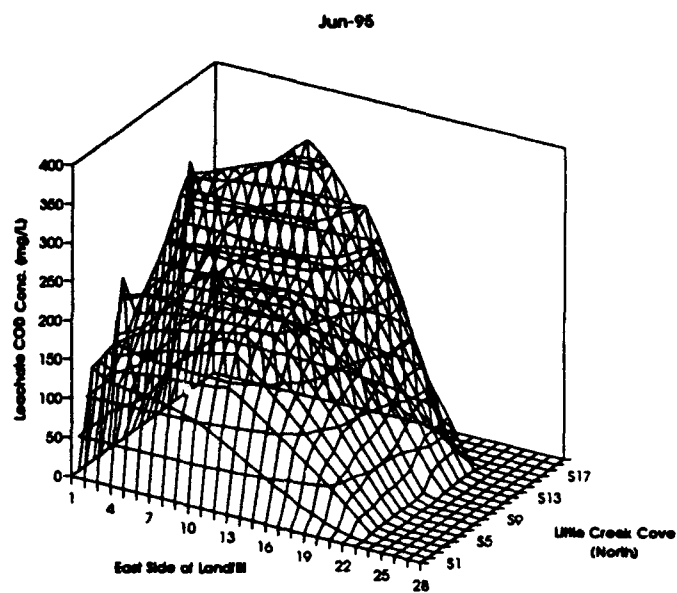


(i)

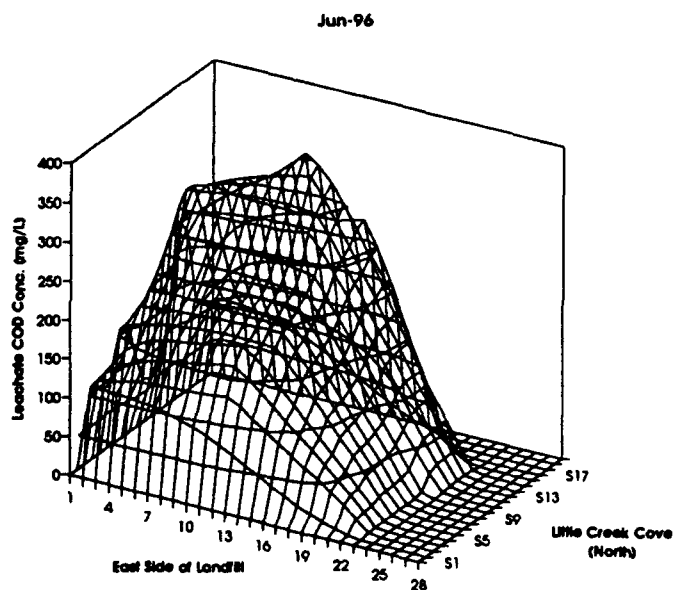


(j)

Figures F4(k) - (l). UNMOC model results for $R_f = 1$, no degradation and $K = 335$ m/d.



(k)



(l)

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